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A STUDY ON THE FUNCTIONAL PROPERTIES OF TARO STARCHES FROM TONGA

PALATASA HAVEA

1993

A STUDY ON THE FUNCTIONAL PROPERTIES OF TARO STARCHES FROM TONGA

A Thesis

presented in partial fulfilment of the

requirements for the Degree of Master of Technology

in Food Technology at Massey University

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ABSTRACT

This study compared the functional properties of three taro starches extracted from selected cultivars, one from each of the three most commonly grown taro genera in Tonga. The selected cultivars were *Alocasia macrorrhiza* var '*Fohenga*', *Colocasia esculenta* var '*Lau'ila*', and *Xanthosoma saggitifolium* var '*Mahele'uli*'. Cassava starch, a commercial product from Thailand, was studied together with the taro starches for comparison purposes.

Freshly harvested taro corms/cormels were peeled, washed, ground into pulp. The taro pulp was washed with excess water and filtered with a cheese cloth. The solid pulp was discarded, and the water-starch mixture (starch milk) was collected in a settling tank. The starch was held for 10-24 hours to allow the starch to settle, and then the supernatant liquid was discarded. The *Xanthosoma* starch was successfully isolated using this method. For the *Alocasia* and *Colocasia*, the starch could not be isolated from the starch milk due to the presence of a mucilaginous material, and it was separated using a bowl centrifuge. The starches were dried, in a hot-air drier and then purified to remove trace of protein, fat, and fibre.

All the taro starch granules were similarly polygonal in shape but the granule sizes were different. The *Xanthosoma* starch granule size (5-30μm) was similar to that of cassava starch granules (5-35μm). The granule sizes of *Alocasia* (0.5-3μm) and *Colocasia* (0.5-6μm) were very small, smaller than rice starch granules. The amylose contents, determined using an iodometric blue value colorimetry method, were 12.1, 13.6, 19.8, and 27.4% for *Alocasia, Colocasia*, cassava, and *Xanthosoma* starches respectively.

The gelatinization temperatures for the starches were determined using sensory evaluation, hot stage microscopy, Brabender Amylograph, and Differential Scanning Calorimetry (DSC) methods. The gelatinization temperatures were approximately 69, 70, 75 and 80°C for cassava, *Alocasia*, *Xanthosoma* and *Colocasia* starches respectively. The gelatinization temperature ranges for *Xanthosoma* and *Colocasia*

were similar to that of cassava starch, but *Alocasia* starch showed relatively wider temperature range. The viscosity of the *Xanthosoma* gelatinized starch paste was much higher than the other starches but showed greater breakdown on heating.

The strengths of the starch gels were determined by measuring the rheological modulus G* of the gels using a Bohlin Rheometer, and the penetration strength test using an Instron. Both tests showed that the *Xanthosoma* starch produced a much stronger and higher viscosity gel than all of the cassava, *Alocasia* and *Colocasia* starches which produced gels with similar strength. The relative order of gel clarity from qualitative sensory evaluation, from highest to poorest clarity, was cassava, *Xanthosoma, Colocasia*, then *Alocasia*.

The storage stability of the starch gels was evaluated by studying the crystallisation using DSC, and measuring the syneresis occurring during storage at 5 and 22°C. The *Xanthosoma* starch gel was extremely susceptible to crystallisation and syneresis during storage, compared with cassava, *Colocasia*, and *Alocasia* gels which had similar stabilities on storage. The freeze-thaw stability of the starch gels was studied by subjecting the starch gels to repeated freeze-thaw cycles. The *Xanthosoma* starch gel was extremely unstable with freeze-thaw treatment. The *Alocasia* and *Colocasia* starch gels were similar to cassava starch gel which was more stable with freeze-thaw treatment.

The *Xanthosoma* starch, because of extremely high viscosity and gel strength, could be use in food products that need high viscous texture but require no further storage. The *Colocasia* and *Alocasia* starches, because of high digestibility due to very small granule sizes can be used in baby food formulations, which are either heat treated or frozen.

Acknowledgements

I wish to thank my supervisors, Dr. Osvaldo Campanella and Professor Mary D. Earle, for all their valuable guidance, time and encouragement provided throughout this research work.

I also wish to thank the staff of the Food Technology Department, Massey University, in particular, thanks to Mr John O'Connor, Mr Hank Van Til, Mr Steve Glasgow, Mr Byron McKillop, and Mr Alistair Young for their assistance in many parts of the laboratory work.

This thesis is dedicated with many thanks to my wife, Sesimani (and Baby), for her patience, encouragement and never ending moral support during the course of this work. Thank you so much for handling most of the hardship of pregnancy by yourself, allowing me to proceed with this research work. Thank you love!

I would like to thank many people who helped during this research work. In particular:

* Many thanks to Samiu and 'Api Taufa for continuously supplying food and daily needs during the busy time of this course.

* Many thanks to my brother Ma'u and family (Lesley, Ma'u Leka, Loleini, Taufa Leka, Mosese Leka, and Palatasa Leka) for their help during the time I spent in Tonga for part of the course.

* Thanks also to Kelepi Mailau, Mosese Taufa, 'Amanaki Paea, Mipa and all the friends who helped in the starch extraction process in Tonga.

* Many thanks also to Mr and Mrs Morgenstern for their hospitality and help during a trip to Christchurch for part of the course.

* Many thanks also to the Naulivou family (Sione, Janice, and Rachel) for their help in preparing this Thesis.

Lastly, I would like to thank the Ministry of Foreign Affairs and Trades, for funding this work.

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CHAPTER ONE
INTRODUCTION

The economy of Tonga relies largely on agriculture and fishery. The fishing industry is seen to be relatively underdeveloped as it operates mainly to supply the local market with virtually no export and has very little impact on the country's economy. The agricultural industry, on the other hand, has made significant impact on the economy due to the export of several agricultural products. These include vanilla, coconut products, squash pumpkin, water melon, and vegetables.

Other than vanilla and coconut, all these produce are exported in their fresh form without further processing. Vanilla is sun dried, with relatively little or no technological method involved, before it is exported. Coconut processing has phased out of the country's economy since the last drop of the coconut oil price in the world market several years ago. So the employment of local resources, including the low labour cost, in commercial processing is virtually non-existent in Tonga. However, this is an area with tremendous potential for industrial development in the country. There are various potentially important commercial crops, eg. cassava, taro, and banana, which could be employed in industrial manufacturing of commercial products.

Cassava is established in the world market as a source of commercial starch. Cassava starch has found a wide range of industrial applications in both food and non-food industries (Balagopalan et al., 1988). Banana has also been a significant commercial crop in the world market for many years. It is largely consumed as fresh fruit but it is also widely used for production of various commercial products such as banana chips, fruit leather, and food flavours.

Taro is insignificant in the commercial scene when compared with both banana and cassava. This study focuses on evaluating the potential of taro as a raw material to be used in manufacturing of commercial products.

1.1 Taro Production and Uses in Tonga

In Tonga, there are three most commonly grown genera of taro: *Colocasia esculenta, Xanthosoma sagittifolium*, and *Alocasia macrorrhiza*. There are many cultivars of each genus grown in the country.

It is estimated that more than 65% of the cultivatable land in Tonga is not cultivated. Taro is cultivated mainly for local consumption and to meet the demand of the small local market, and this accounts for less than 5% of the cultivated land. Currently, the largest commercial crop in Tonga is the squash pumpkin which is exported to Japan. The squash pumpkin accounts for about 70% of the cultivated land, eighty thousand tons of fresh pumpkin are exported and about thirty thousand tons of rejects per year are fed to pigs or wasted. These estimations imply that development of commercial crops like pumpkin and taro to a reasonably large scale is achievable in Tonga, and that there is land for agricultural development.

In Tonga, taro is similar to cassava in being the most commonly grown staple food crop. There is no data available on the average taro yields in Tonga. One would expect that the yields would be similar to those in other countries of the Pacific. For *Colocasia*, the yields are 20-30 t/ha/year in Hawai'i (Wang, 1983) and 10-30 t/ha/year in Fiji (Sivan, 1984). There is no data available on yields for both *Alocasia* and *Xanthosoma*. It has been mentioned, however, that the yields for *Xanthosoma* are higher than that for *Colocasia* (Bradbury and Holloway, 1988). One would also expect the *Alocasia* to have higher yields because of relatively large stems.

It has been reported that taro is used in many different ways among different cultures and countries (Maga, 1992). Most of the taro products are not produced commercially. Taro is normally processed in domestic settings and usually peeled, washed, and then simply boiled, steamed, baked or fried (Wang, 1983) and then consumed either alone or in combination with meat and vegetables as part of an every-day meal in most countries of the Pacific. Taro corms can also be grated after peeling and washing, and used (either raw or in dried form) as an ingredient in

preparation of various traditional delicacies (Havea, 1992). Wang (1983) reported that taro in dried form can also be mixed with corn meal and made into bread or into a sweet dessert.

The leaves of the *Colocasia* varieties and the new leaves of the *Xanthosoma* varieties are usually boiled together with meat or fish in coconut cream. This is then eaten with cooked cassava, taro, yam or sweet potatoes as part of a meal in most of the Pacific islands. A more traditional way of cooking this dish is the wrapping of taro leaves, meat, coconut cream, onions and other spices in banana leaves and then baking in an " 'umu" (Havea, 1992). This is a favourite dish in Tonga and other Pacific countries.

Although the commercial use of taro is very limited, a wide range of taro based products could be produced commercially which could be of major impact in the economy of many parts of the world (Maga, 1992). Currently, commercial taro products come mainly in the form of poi and taro chips. Just recently, Western Samoa started exporting canned taro leaves, "palusami", to the New Zealand market. This may be discontinued due to a dangerous disease that destroyed the taro leaves in Western Samoa, in the middle of 1993.

Poi is made from cultivars of *C. esculenta*. The corms are pressure cooked, peeled, ground, strained to remove fibrous material, and then mixed with water to obtain a paste with 30% total solid. This is a ready-to-eat product, it can be eaten fresh or it can be canned. It is sold in the United States market in the form of a canned purple-grey paste. It is well known for its consistency, high digestibility, and non-allergic properties (Wang, 1983).

In making taro chips, different varieties of taro can be peeled, sliced, and deep fried in the same manner as in the manufacture of potato chips (Murray, 1977). There are various forms of taro chips available in the world market. Maga (1992) reported that in various part of the world, taro corms are peeled, crushed, mixed with other ingredients, formed into patties or slices, cooked and then dried.

Currently, there is no report of commercially produced dried taro products, but various studies have shown that dehydrated taro products can come in various forms including slices, flour, and flakes (Moy et al., 1977; Moy et al., 1980; Wang, 1983; Maga, 1992). Moy et al. (1980) reported that different forms of dehydrated taro can be produced using air, solar, and freeze-drying techniques. Nip (1978) demonstrated that taro flakes can be successfully produced using a drum drying technique. Taro flour can be produced in the same way that cassava flour is produced and can be used as an ingredient in various bakery products including breads, cakes, and biscuits (Maga, 1992). Wang (1983) reported that dehydrated products containing taro, similar to corn meal or grits, have been prepared by roasting sliced or shredded taro, and various dry breakfast foods using taro as a base have also been successfully prepared.

There is no report of commercial extruded taro products in the market (Maga, 1992). Moy et al. (1980), however, demonstrated that taro flour can be successfully extruded, either alone or with the addition of 15% mung bean flour to form pasta-like products such as taro rice, noodle and macaroni. There has been no report on the high-temperature extrusion properties of taro, but because of its high starch and low fat/protein content, it may be successfully extruded to produce an expanded snack (Maga, 1992).

Despite these possible applications, the use of taro as a raw material for commercially produced products is very limited (Bradbury and Holloway, 1988; Maga, 1992; Moorthy et al., 1993). This may be attributed to strong research programs that have developed around other root tubers such as sweet potato and cassava (Maga, 1992).

It has been mentioned elsewhere (Havea, 1992) that cassava starch processing is commonly practised in Tonga on a domestic level. Provided that there are suitable applications for taro starch at a commercial level, a starch processing plant could be set up to extract starch from both taro and cassava. This sort of development would certainly make a positive impact on the economy of the country.

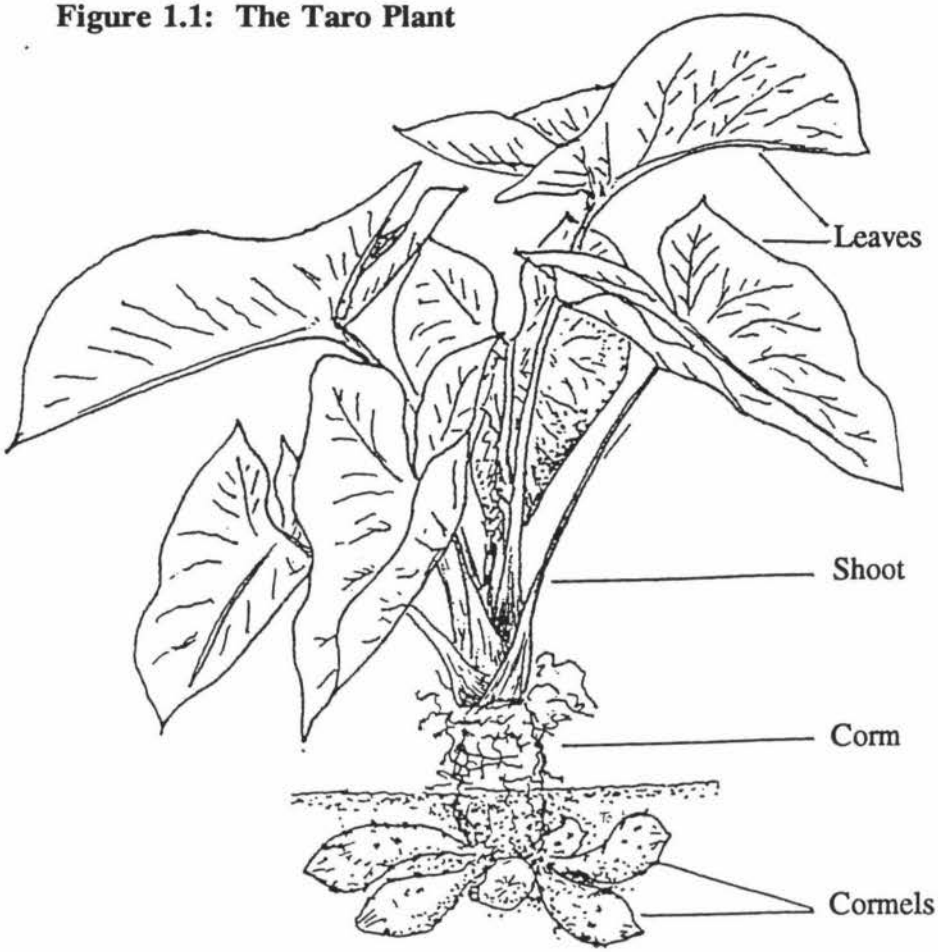
1.2 Taro Botany

Taro belongs to the Araceae family and it consists of more than 100 genera and 1,500 species (Kay, 1973; Plucknett et al., 1985). Taro is grown, as well as other root tubers such as cassava, sweet potato, and yam, in many countries of the tropical world. It is a popular staple food and it contributes a major part of human diet in countries including the Caribbean, Hawai'i, the Solomons, American Samoa, the Philippines, Fiji, Sri-Lanka, India, Nigeria, Indonesia, New Hebrides, Tonga, Niue, Papua New Guinea, and Egypt (Okonkwo, 1987).

Many cultivars of taro can be grown in a wide range of climatological conditions throughout the world (Bradbury and Holloway, 1988). Taro *Colocasia esculenta* cultivars have been reported to be the most important (Georing and DeHaas, 1972; Bradbury and Holloway, 1988; Maga, 1992), and are most widely grown throughout the world. This may be attributed to better yield and shorter maturity time (Bradbury and Holloway, 1988) when compared to other cultivars of taro. The three most commonly grown genera of taro in the South Pacific are *Colocasia, Xanthosoma,* and *Alocasia* (Bradbury and Holloway, 1988). The taro plant consists of three main parts - the main corm, cormels, and the shoots and leaves, as shown in Figure 1.1. Details on the taxonomy, anatomy, morphology, physiology, phytochemistry, and agronomy of taro can be found in Wang (1983).

The edible parts of taro are the leaves, corms and cormels. It has been reported, however, that the shoots of some cultivars of taro are widely used as a green vegetable in some cultures of the Pacific (Standal, 1982; Parkinson, 1984). Acridity is the factor determining the edibility of various parts of taro (Bradbury and Holloway, 1988). For most cultivars of *Colocasia,* both old and young leaves are used as a green leafy vegetable in most of the Pacific countries. For most cultivars of *Xanthosoma*, only the young leaves are used as green leafy vegetable. The older leaves are acrid. The leaves of most cultivars of *Alocasia* are highly acrid and are not used as green leafy vegetable (Standal, 1982).

Figure 1.1: The Taro Plant



The corms or the cormels, depending on the genera, are a good source of starch. The corm of most of the *Colocasia* cultivars are the edible parts which are widely eaten as a carbohydrate source. The cormels are not usually acrid but are often too small. However, some cultivars of *Colocasia* have relatively large cormels which are also eaten as a carbohydrate source (Okonkwo, 1987). The cormels of *Xanthosoma* cultivars are the edible parts. The main corms are usually acrid and the flesh remains hard when cooked. They are often used for animal feed in the countries of the Pacific. The stems, main corms, of *Alocasia* (giant taro) are the edible parts. The cormels are usually too small and highly acrid. The thick skin layer of *Alocasia* is highly acrid and is removed before cooking. If the flesh is also acrid, then special cooking techniques are required before it can be used (Sakai, 1983).

Food compositional analysis has focused only on edible parts of a given cultivar of taro. The fact that some parts are not edible because of acridity has been taken for granted, and so there is no report on the starch content of the non-edible parts of the taro. When referring to the composition or starch content of taro in this study, it is referring to that of the corms, in the case of *Colocasia* and *Alocasia*, and cormels in the case of *Xanthosoma*, unless otherwise noted.

1.3 The Chemical Composition of Taro

The chemical composition of various cultivars of taro has been well documented (Onwueme,1978; Chowdhury and Hussain, 1979; Standal, 1982; Wills et al., 1983; Parkinson, 1984; Tamate and Bradbury, 1985; Bradbury et al., 1985; Bradbury and Holloway, 1988). Table 1.1 presents compositional analysis of corms and leaves of taro (*C. esculenta*) from different sources.

The corms of taro *Colocasia* cultivars had a high moisture content (67-87%). On a dry basis, however, starch was the major component (75-80%), followed by fibre (5-11%), protein (3-11%), and sugars (3-4%). The taro leaves had 81-88% moisture content. On a dry basis there was a lower proportion of carbohydrates (38-50%) which were probably combinations of starch and sugars (and fibre as reported by Parkinson, 1984), significant amounts of protein (21-40%) followed by fibre (16-34%), and ash (10-15%).

There can be considerable variations in taro composition even within the same cultivar growing in different locations. The variations may be attributed to several factors including soil fertility and climatological conditions (Maga, 1992). Wills et al., 1983, showed that the taro composition varied considerably with maturity, moisture decreased from approximately 82 to 62% and starch increased from 10.7 to 30%, between the maturity periods of 14 to 60 weeks. This information shows that in extraction of starch from taro, maturity is a critical factor in obtaining the maximum yields.

Table 1.1: Taro (*C. esculenta*) composition of corms and leaves from different sources (Bradbury and Holloway, 1988)

	Taro corms					Taro edible leaves		
	Bradbury/ Holloway (1988) (a)	Wenkam (1983)	Sth Pac. Comm. (1983)	Standal (1983) (b)	Willis et al. (1983) (c)	Bradbury/ Holloway (1988) (d)	WenKam (1983)	Standal (1983) (b)
Moisture %	69.1	72.4	-	75	66.8	85.4	87.5	81.0
Energy (Kj/100 g)	480	439	470	376	509	114	151	260
Protein %	1.12	1.48	2.0	2.7	1.2	4.2	5.0	4.2
Starch %	24.5	-	-	-	26.2	0.07	-	-
Sugar %	1.01	-	-	-	1.0	0.92	-	-
Carbohydrate %	-	24.8	26	20	-	-	4.8	9.5
Dietary fibre %	1.46	-	-	-	3.8	5.03	-	-
Crude Fibre %	-	0.61	-	0.7	-	-	2.0	3.3
Fat %	1.10	0.11	-	0.15	0.3	0.61	0.74	1.7
Ash %	0.87	1.20	-	0.8	1.0	1.58	1.9	2
Tot oxalate (mg/100 g)	65	-	-	-	36	426	-	-
Ca. oxalate (mg/100 g)	43	-	-	-	-	400	-	-
Minerals (mg/100 g)								
Ca	32	23	25	38	19	182	107	250
Free Ca	10	-	-	-	-	24	-	-
P	70	69	-	64-140	-	61	60	80
Mg	115	20	-	-	28	90	35	-
Na	1.8	12	-	8	1	7.9	2	11
K	448	323	-	530	340	487	437	1240
S	8.5	-	-	-	-	24	-	-
Fe	0.48	1.7	1.0	0.8-1.7	1.1	0.62	2.3	-
Cu	0.20	-	-	-	-	0.15	-	-
Zn	3.6	-	-	-	1.7	0.66	-	-
Mn	0.34	-	-	-	-	4.5	-	-

Table 1.1: Continue

	Taro corms					Taro edible leaves		
	Bradbury/ Holloway (1988) (a)	Wenkam (1983)	Sth Pac. Comm. (1983)	Standal (1983) (b)	Willis et al. (1983) (c)	Bradbury/ Holloway (1988) (d)	WenKam (1983)	Standal (1983) (b)
Al	0.39	-	-	-	-	1.81	-	-
B	0.09	-	-	-	-	0.36	-	-
Vitamins (mg/100 g)								
Vit A (ret + β-car/6)	0.007	0	-	0.02	-	-	0.50	7.3
Thiamine	0.032	0.14	0.10	0.09	-	-	0.14	0.16
Riboflavin	0.025	0.02	0.03	0.03	-	-	0.31	0.3
Nicotinic acid	0.760	0.44	1.0	0.6	-	-	1.0	1.6
Pot. Nic. Acid (Trp/60)	0.19	-	-	-	-	1.0	-	-
Vit C	15	4	5	0-10	-	-	37	12-140
Vit D	0	-	-	-	-	-	-	-
Limiting amino acids and score								
First	Lys 66	-	-	Lys 66	-	Leu 57	-	-
Second	Thr 94	-	-	His 92	-	Lys 62	-	-
Tryp. inhibitor (TIU/g)	13.6	-	-	-	-	0	-	-
Edible matter, prop. of amount purchased	-	0.86	0.80	0.81	-	-	0.65	0.55

a = 71 samples from Fiji, W. Samoa
b = From India and Philippines
c = 36 samples from 22 cultivars of PNG Highlands
d = 10 samples from Fiji

There were also differences between the compositions of different taro cultivars. Tables A1, A2, and A3 of the Appendix 1 show the compositions of various cultivars of *Colocasia, Xanthosoma*, and *Alocasia* (Bradbury and Holloway, 1988). It can be seen from the tables in the Appendix 1 that the three genera of taro (*Colocasia, Alocasia*, and *Xanthosoma*) fulfil a similar nutritional requirement. Generally, the edible corms or cormels are a good source of energy, starch, fibre and minerals. The edible leaves are a good source of vitamins, protein and mineral. The traditional way of consuming taro in the Pacific countries, where cooked taro corms or cormels are eaten with taro leaves cooked together with meat or fish and vegetables, is a good way of maintaining a well balanced diet.

A general comparison of the main components of the most commonly grown taro genera in the South Pacific is given in Table 1.2 (extracted from Appendix 1).

Table 1.2: The main components of Taro corms or cormels (dry basis)

	% Dry basis			
Genera	**Starch**	**Fibre**	**Protein**	**Sugars**
Alocasia	66-78	6-10	2-6	2-3
Colocasia	80-88	3-5	3-4	1-3
Xanthosoma	77-82	3-4	3-5	1-3

It can be seen that giant taro *Alocasia* contained less starch (66-78%) than both *Colocasia* (80-88%) and *Xanthosoma* (77-82%) on a dry basis. The general composition was very similar for both *Colocasia* and *Xanthosoma*. It is clear from this table also that the major component of taro corms or cormels is starch. Utilization of taro as a raw material in industrial processing would be based on its starch content.

The results also showed that there were significant variations of compositions within cultivars of taro. These variations were most likely due to samples analysed at different stages of maturity.

The starch content of taro is similar to that of other tuber crops used as sources of commercial starches. Table 1.3 compares the starch contents of taro genera to those of cassava and potato which are used for commercial starch production.

Table 1.3: Starch contents of various root tubers (% dry basis)

Root crop	Starch content	Source
Cassava	80-86	Bradbury & Holloway (1988)
	91	Knight (1969)
Alocasia macrorrhiza	66-78	Bradbury & Holloway (1988)
Colocasia esculenta	80-88	Bradbury & Holloway (1988)
Xanthosoma sagittifolium	77-82	Bradbury & Holloway (1988)
Potato	75-80	Knight (1969)

It can be seen that taro, like cassava and potato, contains considerable amount of starch (66 - 88%) depending on the variety. Because the starch content of taro is sufficiently high, and is the same as that of cassava (Moorthy, 1991), there is a high potential that taro could be a significant source of commercial starch.

1.4 Taro Starch

Industrial applications for tuber starches are increasingly recognized. Taro starch could find a variety of applications in many industries. Various studies on taro *Colocasia* have suggested various potential features of the starch. Because of its small granule size, it is easily digestible, and so can be used in baby foods and diets of people who are allergic to cereals and children sensitive to milk (Wang, 1983). Griffin and Wang (1983) reported that taro starch can be used in cosmetics like face powder. Higashihara et al. (1975) reported that taro starch is a suitable filler in biodegradable plastics.

Having shown that taro is a potentially important commercial crop, and that starch is its major component, it was desirable to consider investigations into the functional properties of taro starch. Starch has been extracted from different cultivars of taro and the functional properties studied.

A literature review has shown that the functional properties of the commonly used starches like cassava, corn and wheat starches were established through extensive scientific research, but there is obviously a lack of information on the functional properties of taro starch, especially of different cultivars. Most of the studies on taro have been on the *Colocasia*

cultivars, with very little or no mention of *Alocasia* and *Xanthosoma*. It was therefore decided that a selected cultivar from each of the commonly grown genera of taro in Tonga be used for starch extraction in this study. These cultivars were *Colocasia esculenta* var *"Lau'ila"*, *Xanthosoma sagittifolium* var *"Mahele'uli"*, and *Alocasia macrorrhiza* var *"Fohenga"*. The method of selecting those cultivars is given in Appendix 2.

The aim of this study was therefore to establish the functional properties of taro starch extracted from different cultivars in Tonga. A literature review was carried out to investigate the suitable functional properties of starch that are important for industrial applications, and to consider the different studies carried out on taro starch. An attempt was then made to develop a suitable method of extracting starch from the selected taro cultivars. The extracted starch was used to establish the granule morphological and molecular structures of each starch. The gelatinization properties of the test starches were studied using various tests. The gelation and storage properties of the starch gels were also determined using different methods. From these studies, recommendations on the suitability of taro starches for industrial applications were developed.

CHAPTER TWO
LITERATURE REVIEW: THE FUNCTIONAL PROPERTIES OF TARO STARCH IN COMPARISON TO OTHER INDUSTRIAL STARCHES

2.1 Introduction

Starch is widely used in many applications not only in the food industry but also in other industries such as paper and textiles. The most common sources of commercial starches are the tuber starches (Balagopalan et al., 1988), such as cassava and potato starches, and cereal starches (Lund, 1984), such as corn and wheat starches.

Starches are used in the food industry in many ways. They are used as thickeners in products such as gravies and pie fillings; binding agents in products such as formed meat and extruded foods; gelling agents in products such as confectionary and desserts; and many others.

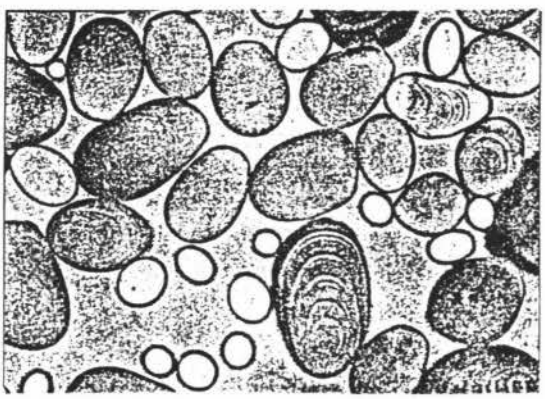
The wide range of applications provided by different starches in the food industry are not primarily based on the starches' nutritional values, but on their functional properties. Most of these functional properties are revealed in foods after the starches have undergone the process of gelatinization. The suitability of a given starch for particular industrial applications is based on the functional properties.

Taro has been shown to have the same starch content as the other tubers, used as sources of industrial starches such as cassava and potato (Chapter 1), and to have potential for industrial applications. Taro, however, has not been used as a source of industrial starch due to lack of information on the starch's functional properties. This chapter reviews the functional properties of industrial starches in relation to those established about taro starch.

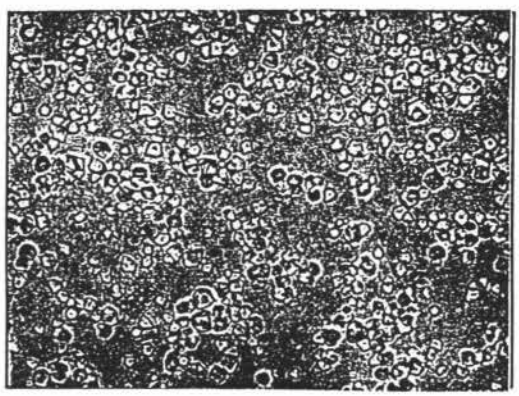
2.2 Starch Granules: Morphological and Molecular Structure

Starch exists in plants in the form of microscopically small grains (Sterling, 1968). The size and shape of starch granules are characteristics of botanic origin. Potato starch granules are large, oval and have oyster-like striations. Corn starch granules are mostly polygonal in shape. Rice starch granules are irregular in shape and relatively small. Figure 2.1 shows the characteristic granule sizes and shapes of potato and rice starches (Knight, 1969). When examined microscopically under polarised light, the intact granules exhibit well define polarization crosses, birefringence patterns, (Figure 2.2).

Figure 2.1: Starch granules of potato and rice starches (light microscopy)

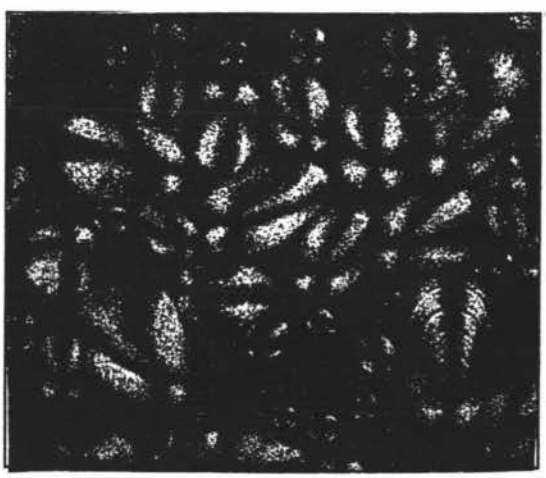


Potato starch granules

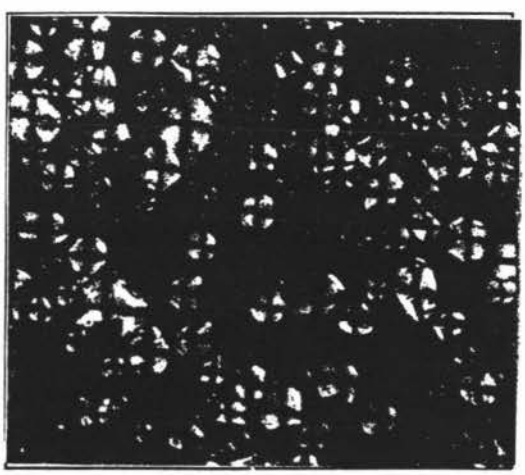


Rice starch granules

Figure 2.2: Starch granules under polarized light



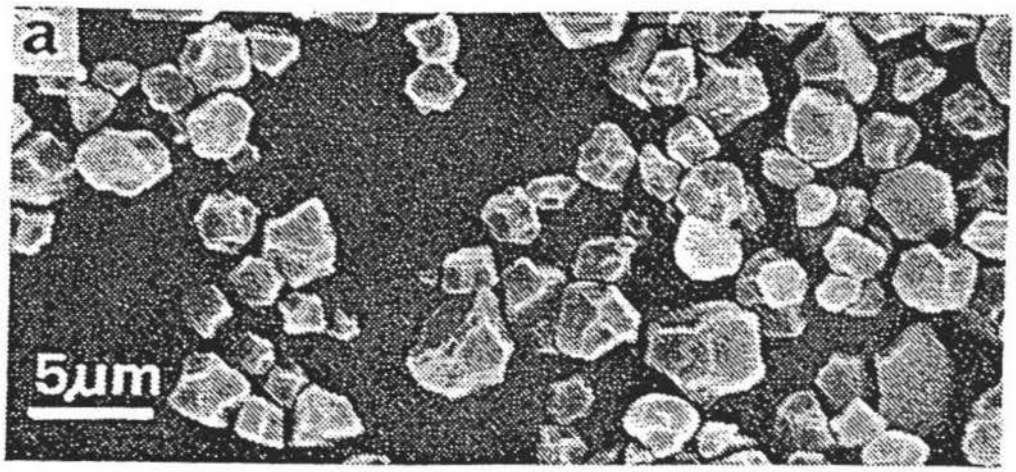
Potato starch granules



Maize starch granules

Figure 2.3 shows scanning electron photomicrographs of taro (*C. esculenta*) starch granules (Kinjo and Fukuba, 1978). The granule size has been reported to be variety dependent (Georing and DeHaas, 1972). However, taro starch granules have smaller general size than those of cereal and most other root tuber starches.

Figure 2.3: Taro (*C.esculenta*) Starch Granules



It can be seen (Figure 2.3) that taro starch granules are polygonal in shape, similar to that of rice starch, but generally smaller in size: rice granules have a general size of 3-8 µm (Knight,1969). Table 2.1 (Georing and DeHaas, 1972) compares the granule sizes of different varieties of taro *Colocasia*. The Miyako, Bun Long, and Poitere cultivars have similar general granule sizes to that of rice starch granule. It is striking to note that there is a significant granule size variation not only between various cultivars but also within cultivars. The granule size distribution of many taro cultivars can be seen to be significantly covering a wider size range than other starches. This can be seen as an unique feature of taro starch, with the other starches, such as cassava and potato starches, there is generally a narrow size range, (Moorthy et al., 1993).

Table 2.1: Starch granule size of different cultivars of *Colocasia* (Georing and DeHaas, 1972).

Variety	Smallest	Largest	General size
	μm	μm	μm
Uramata	0.5	6.5	1.5-4.0
Yen No. 608	0.75	5.5	2.0-4.0
Yen No. 606	1.0	4.0	1.5-2.5
Yen No. 830	0.6	3.0	1.5-3.0
Yen No. 612	1.0	4.0	1.5-3.5
Lliuarua	0.75	3.5	1.5-3.0
Miyako	1.5	7.5	2.5-6.0
Bun Long	1.0	7.5	3.0-6.6
Poitere	1.5	6.0	2.0-5.0

Because of the small size of the granules, taro starch has been considered to be easily digestible (Wang, 1983). Sugimoto et al. (1986) compared the digestibility of taro starch to that of yam (granule size of about 16-18 μm), by treating the starches with hog pancreatin for 24 hour reaction time. They discovered that the percentage degradations for taro and yam starches after 24 hours were 37.9% and 17.4% respectively. It should be noted, however, that this result may be of little significance in the food industry, since starches are applied in food systems mostly in their gelatinized form.

Starch is made up of two structurally distinct polysaccharides: amylose and amylopectin (Morris, 1990). Both polysaccharides are polymers of α-D-glucopyranose units. Amylose is mostly linear, where the glucopyranose molecules are α-1-4 linked, while amylopectin is a branched molecule where there are α-1-6-linkages in addition to α-1-4-linkages. Most starches contain 15 to 25% amylose (Manners, 1979). The ratio of amylose to amylopectin is a characteristic of botanic origin and a major determining factor in the functional properties of starches.

The amylose molecular size is in the range of 200 to 2,000 anhydrous units (Smith, 1982) depending on the source. Since the anhydroglucose units expose an abundance of hydroxyl groups, the amylose molecule imparts hydrophillic properties, giving it an affinity for moisture and dispersibility in water (Wurzburg, 1986). Amylose molecules in solution have the tendency to orient themselves in a parallel fashion,

forming hydrogen bonds between adjacent molecules which may lead to spontaneous precipitation (Balagopalan et al., 1988). This phenomenon is known as 'retrogradation' (Section 2.8.5). Retrogradation is a characteristic property of amylose in dilute solution (<5% for most starches).

There is variable information about the amylose content of taro starch. Georing and DeHaas (1972) suggested that taro contained approximately 50% of the amylose content of cereal starches. Kinjo and Fukuba (1978) reported a 7-10% amylose content of taro *Colocasia*. Sugimoto et al. (1986) reported the amylose content of cultivars referred to as taro (ishikawa-wase) and taro (takenokoimo), both are varieties of *Colocasia*, to be 13.5% and 10.8% respectively.

Table 2.2: Total and soluble amylose contents of *Colocasia* starch (Moorthy et al., 1993).

Variety	Granule size μm	Total amylose (%)	Soluble amylose (%)
C-9	5.19	19.4	8.8
C-46	2.96	16.1	9.3
C-62	4.27	14.5	6.6
C-149	3.06	15.1	8.8
C-189	3.30	14.0	4.4
C-216	3.51	14.5	6.5
C-218	3.39	15.7	8.3
C-220	3.55	17.6	10.7
C-266	3.16	15.7	9.8
C-304	3.20	16.1	7.5

Table 2.2 shows the variations in amylose content of *Colocasia* varieties (Moorthy et al., 1993). The values ranged from 14.0 to 19.4%, and it is interesting to note that C-9, with the largest granule size, had the highest amylose content (19.4%). C-220 had the next highest amylose content and the lowest was observed for C-189. Moorthy et al. (1993) suggested that there was no relationship between granule size and amylose content of taro starches. This is in agreement with Strauss and Griffin (1984).

Amylopectin is a branched polymer containing 94-96% α-1-4 and 4-6% α-1-6 linkages (Hood, 1982). Each branch contains about 20 to 30 anhydroglucose units (Wurzburg, 1986). Molecular weight is of the order of 10^7 to 10^8 (Hood, 1982).

Because of the large size and the branched structure, amylopectin molecules exhibit low mobility in solution and have little tendency to align closely parallel to each other forming hydrogen bonds between them. As a result the amylopectin solution is characterized by clarity and gel stability (Wurzburg, 1986). Amylopectin forms a red-purple colour with iodine reflecting short effective linearity, about 25 glucose units (Pomeranz, 1985).

There is no information on the amylopectin content of taro starches. It is generally considered that determination of the amylose content of a given starch indicates the amylopectin content since starch consists generally of only two main polymers, amylose and amylopectin. Banks and Greenwood (1975), however have reported the existence of up to 10% of a third component in starch. The lack of information on the amylopectin content of taro starch is an indication of limited research carried out on taro.

The ratio of amylose to amylopectin plays an important role in the molecular organisation within the granules. Because of the linear and branched structures of amylose and amylopectin respectively, their orientation within starch granules results in formation of crystalline and amorphous regions (Sterling, 1978). The degree to which each region is formed, depends on the degree of branching or linearity of the starch molecules. If the starch contains high amylose content, the linear molecules align themselves closely to form crystalline regions. A high amylopectin content, on the other hand, results in formation of amorphous regions within the granules. The strength of the hydrogen bonding between molecules within the crystalline regions determines many of the functional properties of the starch granules, particularly their gelatinization properties (Balagopalan et al., 1988).

2.3 Gelatinization Phenomenon

Starch granules are insoluble in cold water (Lund, 1984). When a solution of raw starch is heated, the granules will slowly swell to several times their original sizes (Sterling 1978). At this stage very limited water seeps in and saturates the open inter-micellar areas in the granules (Pomeranz, 1985). When a sufficiently high temperature (gelatinization temperature) is reached, the granules swell markedly and irreversibly to many times (25-30 times) their original sizes (Sterling 1978). This process is known as 'gelatinization'. At this stage the granules lose their birefringence and this process is accompanied by rapid increase in viscosity and paste clarity (Smith, 1982). Upon cooling, the suspension sets into a three-dimensional gel network (Lund, 1984).

The gelatinization temperature is a characteristic of botanic source (Knight, 1969). The gelatinization occurs within a range of about 5 to 10°C (Lund, 1984), hence the gelatinization temperatures for different starches are listed in most literature as temperature ranges. This temperature range may be attributed to the fact that each starch granule has its own unique, characteristic, physical features that give rise to unique gelatinization temperatures (Smith, 1982).

The gelatinization temperature is directly influenced by the intermolecular binding forces within the granules which vary with species (Balagopalan et al. 1988). The higher the internal associative forces within the granules the higher the gelatinization temperature. The gelatinization temperature for cassava is 58 to 70°C, compared to maize, 62 to 72°C (Balagopalan et al., 1988). This indicates that the associative forces between the molecules within the cassava starch granules are less than those between the molecules within the maize granules. The various factors which determine the associative forces include (1) ratio of amylose to amylopectin, (2) molecular weight of the fractions, (3) molecular weight distribution, (4) degree of branching, (5) conformation, and (6) length of the outer branches of amylopectin molecules that can take part in associative linkages (Leach, 1965).

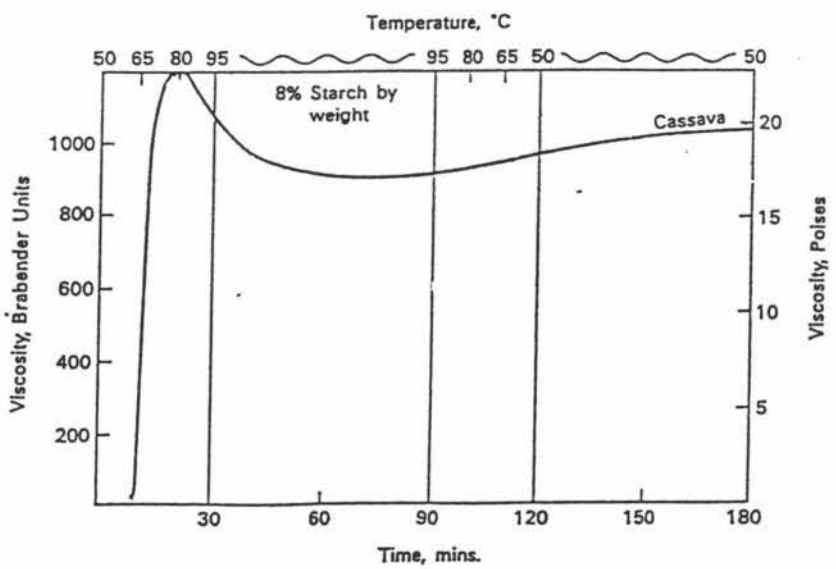
There are variable reports on the gelatinization temperature of taro starches. Kinjo and Fukuba (1978) reported that taro *Colocasia esculenta* starch gelatinized at 72 °C, when studied using pastegraphy. When using the Brabender amylograph the gelatinization temperature of the same starch suspension was found to be 78°C. Sugimoto et al. (1986) reported that the initial temperature for gelatinization, determined by photopastegraphy, was 62°C for taro (ishikawa-wase) and 73°C for taro (takenokoimo), both were cultivars of *Colocasia esculenta.* When using Differential Scanning Calorimetry, DSC, the onset temperatures were found to be 65 and 76°C taro (ishikawa-wase) and taro (takenokoimo) respectively. It seems from these reports that different methods gave different gelatinization temperatures. The work done by Kinjo and Fukuba showed a 6°C difference in the results obtained from the two methods used. This suggests that in comparative studies on gelatinization of various starches, it is important to be consistent in the methodology used, and also in reporting data such as gelatinization temperatures, the method used should be noted. Again the variability among cultivars was also observed for gelatinization temperature.

The swelling of the starch granules during the gelatinization is due to water molecules hydrating and solvating liberated hydroxyl groups. The swelling is initiated by water molecules disrupting the weaker hydrogen bonds in the amorphous areas and the granules continue to swell with progressive hydration (Smith, 1982). As a consequence of severe disruption of hydrogen bonds, the granules will be fully hydrated and eventually collapse; when amylose molecules and hydrolysed linear fractions diffuse into solution (Lund, 1984). Mahanta and Bhattacharya (1989) showed that a significant hydrolysis of starch molecules took place during the gelatinization process in rice starch. Hydrolysed linear fractions of amylopectin molecules, therefore diffuse into the aqueous medium with amylose molecules. Morris (1990) pointed out that even on heating to 100°C there was little evidence for the release of substantial quantities of amylopectin. Thus application of heat to a starch suspension results in a fluid, composed of porous, gelatinized and swollen granules with an amylopectin skeleton, suspended in a hot amylose and linear polymer solution.

The gelatinization process abruptly changes the rheological behaviour of the solution. A simple but empirical way of following the gelatinization of starch is by plotting the changes in viscosity when a stirred suspension of starch is heated and cooled at a uniform rate. This is recorded on a Brabender Amylograph in the starch industry (Smith, 1982). Although there are a number of instruments which have been devised to follow the rheological behaviour, the Brabender Amylograph is the most commonly used method (Havea, 1992). A typical Brabender Amylograph curve (Figure 2.4) for a starch paste gives five points of interest (Balagopalan et al., 1988). They are:

- Peak viscosity, which represents the highest viscosity the starch paste can reach.
- Viscosity at 95°C, which in relation to peak viscosity gives an idea of the ease of cooking of the starch.
- Viscosity after cooking at 95°C for a certain period, which reflects the stability or breakdown of the starch.
- Viscosity of the paste after cooling to 50°C, which is a measure of setback produced by cooling.
- Final viscosity after stirring for a definite period at 50°C, which indicates the stability of the cooked paste.

Figure 2.4: Viscosity behaviour of cassava starch (Knight, 1969)

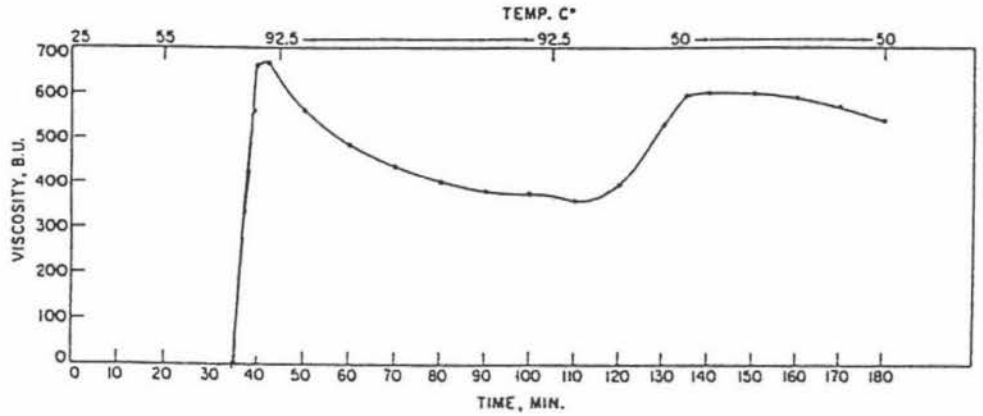


It can be seen that for a given starch, the Amylograph shows an early increase in viscosity followed by a decrease as heating continues and a slow increase on cooling. The increase in viscosity in the early stages is caused by the swelling of the starch granules. The swelling reaches a maximum point at which the granules collapse with further hydration. As heating continues, the granules will collapse which causes the drop in viscosity. The interaction of the extragranular materials and the swelling granules causes the slow increase of viscosity at the later stage of the amylographs (Lund, 1984).

Each raw starch has its own characteristic viscosity-temperature profile. Potato starch, when compared with corn starch, shows an earlier gelatinization, higher peak viscosity and higher breakdown. This shows that the associative forces between potato starch molecules in the granules are relatively weak compared to corn starch. The water molecules are able to penetrate the starch granules much easier, and the granules swell enormously, leading to weakening of associative forces, which in turn makes them susceptible to breakdown (Balagopalan et al., 1988).

Figure 2.5 shows the Brabender curves for taro starches of different varieties of taro *Colocasia* (Georing and DeHaas, 1972). It can be seen that *Colocasia* starches had a single-stage gelatinization. The starches of these taro cultivars showed only a low peak viscosity, extreme granule stability, and small viscosity breakdown. The small viscosity breakdown can be attributed to strong associative forces within the starch granules of *Colocasia* (Moorthy et al., 1993). There were similar pasting temperatures among different cultivars (80 - 86°C).

Figure 2.5: Brabender amylogram of taro *Colocasia* starch, 8% (Georing and DeHaas, 1972).



Georing and DeHaas (1972) reported that *Colocasia* pastes were much more transparent than cereal starch pastes and were extremely stringy. However, it was pointed out that clarity and sol stability of *Colocasia* were relatively poorer than those for cassava paste, and these were also attributed to the strong associative forces within the starch granules of *Colocasia* (Moorthy et al., 1993).

In summary, the starch gelatinization involves the following steps (Lund, 1984):

- granules hydrate and swell to several times their original size
- granules lose their birefringence
- clarity of the mixture increases
- rapid increase in viscosity
- linear molecules dissolve and diffuse from ruptured granules
- upon cooling, the uniformly dispersed matrix forms a gel or paste-like mass

Upon cooling a cooked starch suspension, a three-dimensional gel network is formed. Studies on the composite nature of starch gels have led to a better understanding of the functions of amylose and amylopectin in the formation of a gel network. The

swollen starch granules may break down by shear force, into fragments, microgels, and molecules, because they are susceptible to mechanical shearing (Leach, 1965). Dublier et al., (1987) reported that a starch-based gel system, is a mixture of swollen granules, microgels, and a soluble fraction of macromolecules (amylose).

2.4 Swelling Power

The swelling power varies considerably among different starches. It may be defined as the maximum increase in weight which the starch undergoes when allowed to swell freely in water at a specified temperature. The weight increase is expressed as weight of water per weight of dry polymers (g H2O/g dry polymer) (Kulicke et al. 1989).

A weighed sample of starch is suspended in distilled water in a centrifuge bottle, heated for 30 mins at a specified temperature while stirring, centrifuged, supernatant removed, and the weight of the swollen sediment is determined (Balagopalan et al., 1988). Swelling pattern is usually obtained by plotting the values found at 5°C intervals over the pasting range of the starch. Schoch (1964), however, suggested a standard method where a single measurement is taken only at 85°C. This method is considered to be convenient in comparing the swelling behaviour of different starches. Leach (1965) reported that each species of starch showed a characteristic swelling pattern. This property is dependent on the nature and strength of the micellar network within the starch granules (Balagopalan et al., 1988).

Most starches fall into 3 groups, which follow the order of degree of association (Balagopalan et al., 1988). The cereal starches with the highest degree of association have the lowest swelling power, followed by root starches and then tuber starches. Many cereal starches show two-stage swelling patterns, reflecting the presence of two types of internal associative forces, which probably exist in the crystalline and amorphous regions of the granules (Zuber, 1965). Cassava starch shows a higher swelling power, single stage swelling and a higher solubility, reflecting the lower strength of the associative forces within the granules (Balagopalan et al., 1988).

There is no available information on the swelling power of taro starches. One would expect that it would fall in the same category as that of other tuber starches. For example, it may be similar to that of cassava because of similar amylose content, 14-20% for *Colocasia* (Moorthy et al., 1993) and 16-18% for cassava (Balagopalan et al., 1988). However, this is yet to be determined.

The swelling behaviour of starches is important in understanding their gelation properties. Higher swelling power of starches indicate higher concentration of solubilized amylose molecules and hydrolysed fractions of amylopectin in solution. This higher polymer concentration may give rise to more interpenetration and reassociation of starch molecules resulting in formation of stronger gels.

2.5 Gel Strength

It has been mentioned that on cooling a gelatinized starch suspension of high concentration (>5%) a three-dimensional gel network is formed. It has been mentioned also that formation of the gel network involves recrystallization and reassociation of amylopectin molecules. Balagopalan et al. (1988) reported that these crystalline areas within the swollen granules decide the strength and rigidity of the gel.

Sterling (1960) reported that the elasticity of the starch gels was due to the ability of the gel to be stretched to a certain extent without breaking, and has attributed this property to the portions of macromolecules that lie in the amorphous regions between the crystalline micelles. There is a linear relationship between gel strength and starch concentration (Havea, 1992).

There is very limited information on the gel strength of taro starches and their tendency to undergo retrogradation (Section 2.8.4). Griffin and Wang (1983) reported that taro starch showed very high gel strength, and suggested that it would be suitable for plastic production. This result however, needs further confirmation.

Although gel formation is desirable in many food systems, there are physical changes associated with the processing conditions or physicochemical changes in the food systems which may render undesirable changes to the gel structure. Retrogradation, for example, often occurs when a food system is stored for a long time (Smith, 1982) or undergoes repeated freeze-thaw cycles (Balagopalan et al., 1988).

In starch-based food systems where physical changes or processing conditions are likely to affect the gel strength, it is very important that the gel does not break down, ie. sol stability has to be maximum. The gel stability of cassava starch is much higher compared to cereal starches and hence is preferred for many food products especially when the food has to be stored for a long time (Balagopalan et al., 1988). Different starch modification processes such as cross-linking (Wurzburg, 1986) and derivatization (Smith, 1982) improve the sol stability of many starches.

2.6 Paste Clarity

The clarity of gels formed by starches is often of importance to the food manufacturer from the point of view of 'eye appeal' to the customer. A suspension of starch in water is opaque, but gelatinization of starch granules increases the transparency of the solution. Kite et al. (1963) found that there is a linear relationship between the clarity of the starch paste and the swelling of the granules for all starches. These results were obtained from tests using light transmittance measurement. Root tuber starches such as cassava and sago starches, had a higher paste clarity.

Georing and DeHaas (1972) reported that *Colocasia* pastes were much more transparent than cereal starch pastes and were extremely stringy. However, it was pointed out (Moorthy et al., 1993), that clarity of *Colocasia* starch pastes was relatively poorer than that of cassava paste.

The clarity of starch gels within food products is also greatly influenced by the presence of other materials, such as fruit fibre residues, protein particles, which increase the cloudiness of the pastes (Radley, 1976). Sugars, sodium lauryl sulfate and cetyl trimethyl ammonium bromide increase the paste clarity (Balagopalan et al., 1988).

2.7 Factors Affecting the Gelatinization of Starches

Most of the starch functional properties discussed so far apply to gelatinization of starch-pure water suspensions only. In food systems however, there are factors which are likely to affect the gelatinization process, and hence the functional properties. The processing conditions may apply mechanical shear, pressure or high temperatures which may alter the structure of starch granules hence altering the gelatinization process. Other factors such as limitation of water, change of pH, and presence of other solutes and ingredients will influence the gelatinization of starches in foods. It is critical that in food systems with these varying conditions the starch pastes maintain their desired functional properties. The influence of these factors on starch gelatinization are discussed in this section.

2.7.1 Effect of Moisture

Water must be present in sufficient amounts to hydrate the starch granules and to allow typical starch gelatinization to occur (Biliaderis, 1992). Eliasson (1980) reported that for complete gelatinization, a critical moisture to starch ratio (w/s) is required. Wirakartakusumah (1981) suggested that a w/s ratio of 1.5:1 would be required for complete gelatinization for rice starch (60% moisture, wet basis). In foods such as gravies, sauces, and puddings, there is sufficient water present and gelatinization, swelling and dispersion of starch take place normally. In other foods, such as bread, cakes, snacks, there is limited water available. Normal heating in these cases will result in partial swelling and gelatinization of starch (Lund, 1984; Waniska and Gomez, 1992; Kokini et al., 1992). Swollen and partially gelatinized granules experience deformation in direction of shear in baked products such as bread

and cakes. These granules are an essential component of gas (CO_2) cell walls; without them the gas bubbles coalesce during the baking process (Sandstedt, 1961). In hard bakery products (biscuits, crackers), the starch is mostly ungelatinized due to the small amount of water present in the dough. Therefore, together with fat, it contributes to the shortness texture of these products (Sterling, 1978).

In extruded foods, limited moisture, high shear and high temperature processing causes extensive gelatinization, dispersion, and reorganisation of starch (Waniska and Gomez, 1992). During extrusion, shear force physically tears apart starch granules and allows faster transfer of water into the interior starch molecules (Burros et al., 1987). The loss of crystallinity during extrusion is caused no longer by penetration of water but by mechanical disruption of the molecular bonds by the intense shear fields within the extruder (Waniska and Gomez, 1992). Kokini et al., (1992), reported that under extrusion at low moisture content, a mixture of small amounts of gelatinized and 'melted' starch as well as fragments of starch exist simultaneously.

2.7.2 Effect of pH and Other Solutes

When a starch-water suspension is heated at neutral pH under appropriate conditions, it will result in a short, heavy bodied texture. If this same starch is heated at an acidic pH, below pH 3.5, it will quickly gelatinize with substantial loss of granular integrity, yielding a long texture with a thin viscosity (Light, 1990). At alkaline pH, the gelatinization rate is greatly increased. Alkali has been widely used in non-food applications to induce starch swelling at moderate temperature (Wootton and Kensington, 1989). The effect of extreme alkali or acidic pH may be attributed to the effect of hydrolysis that both acid and alkaline induce on starch molecules.

Sucrose has been reported to have a restrictive effect on the extent of gelatinization of wheat starch (Wootton and Bamunuarachchi, 1980; Light, 1990). Several explanations have been suggested for this phenomenon including competition between starch and sucrose for available water, sucrose inhibition of granular hydration and sucrose-starch interaction (Lund, 1984).

2.7.3 Effect of Lipids and Proteins

Both of these ingredients increase the gelatinization temperature of starch. They tend to coat the granule, limiting the water penetration and thus hydration and swelling (Light, 1990). Starch has been reported to form complexes with lipids and surfactant (Lund, 1984). Early studies postulated that surfactant enters the starch granules (Schoch, 1965; Miller et al., 1973). This observation was confirmed by Ghiasi et al. (a) (1982). Ghiasi et al. (b) (1982) suggested that there may be an adsorption effect of surfactant on the surface of starch granules. Lipid and surfactant-amylose complexes delay the release of solubles, the deformation, and the collapsing of the starch granules (Ghiasi et al. (b), 1982; Lund, 1984). This is caused by preventing hydration of micellar region by the lipid-surfactant complexes (Pomeranz, 1985).

There is no available information on the effects of these factors on taro starch gelatinization. One would expect these factors to have similar influences on taro starch as on other starches. However, defined details and possible deviation from these observations are yet to be determined. This is certainly an area that needs to be defined for taro starch.

2.8 Relationships of Functional Properties to the Use of Different Starches in Foods

An aqueous starch dispersion in a food system may be surrounded by a wide range of environmental molecules including water, lipids, proteins, vitamins, other polysaccharides and other molecules used industrially. While interacting with these environmental molecules, starches are required to perform their desirable practical functions which are mainly to give viscosity, solution stability, suspendibility, emulsifying action, gelation without syneresis, and compatibility with proteins, other polysaccharides, or other ingredients present (Whistler, 1973). Furthermore, starches may be undergoing various changing processing conditions, eg. freeze-thaw cycles, through which they are required to maintain their functional properties. The

capability of starches to maintain their desirable functional properties during these various changing conditions is a major concern in the food industry.

2.8.1 Starch Modifications

The functional properties of most starches have been reported to be unstable under many processing conditions (Wurzburg 1986; Light, 1990). The viscosity of potato, tapioca and waxy starch pastes is drastically thinned under high shear. Most unmodified starch pastes undergo retrogradation on freeze-thaw processing. Therefore many industrial starches are treated with various modification processes. These modification processes result in production of starches that suit particular applications and withstand different processing conditions. In general terms, the modification processes alter the molecular and/or granular structure of starches which in turn alters their gelatinization properties.
These modification processes have been well documented. Details on these processes can be found in Pomeranz, 1985; Jerowenko, 1986; Wurzburg, 1986; and Light, 1990.

There is no information on modification processes of taro starch. This is also another area that needs to be studied.

2.8.2 Thickening Agents

Starches are commonly used in foods as thickeners. They impart thick texture and consistency in foods such as sauces, cream soups, and pie fillings. The use of unmodified cereal starches such as corn, rice and wheat faces the problem of high tendency to retrograde (Pomeranz, 1985). Cross-bonded starches are widely used because they provide the desired thickening properties with elimination of retrogradation problems.

Starch thickeners must be stable under high temperatures, when employed in canned foods which undergo sterilization by autoclaving or retorting. High swelling potato

and sorghum starches are drastically thinned and solubilized. Corn starch is substantially solubilized, though subsequent congelation of its linear fraction gives an apparent high viscosity. Cross-bonded starches maintain viscosity and solubility under high temperature conditions. Starch thickeners must not thin excessively under conditions of shear and agitation. Cross-bonded starches have been shown to resist these conditions (Pomeranz, 1985).

2.8.3 Emulsifying and Stabilizing Properties

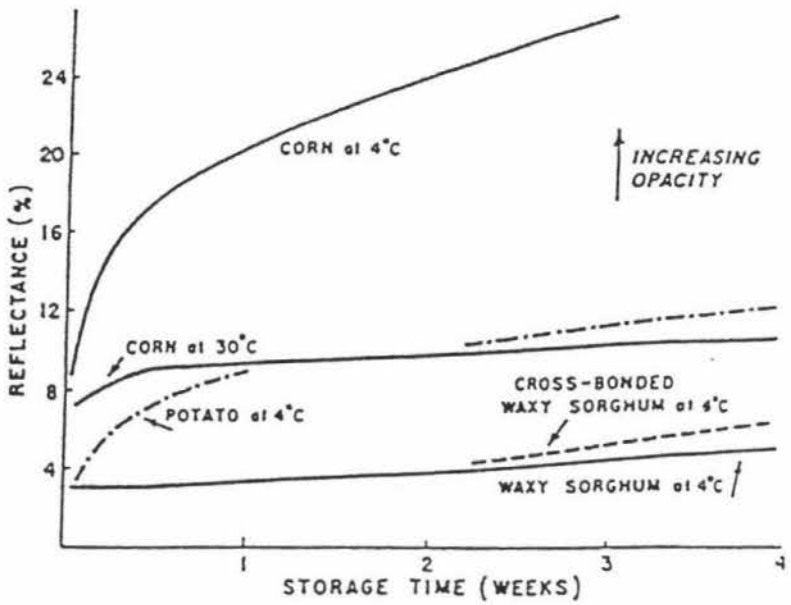
Starch is not a highly efficient emulsifying agent, primarily because it lacks the polyelectrolyte character necessary for emulsion stability. However, starch phosphates are good stabilizing agents. Starch phosphates are produced by using sodium trimetaphosphate and phosphorus oxychloride to cross-link starches in which a phosphate diester bond covalently links starch molecules. Because of their ionic properties, starch phosphates are good emulsifying agents. Starch phosphates are relatively clear, stable, thickening agents with excellent freeze thaw stability (Solarek, 1986). They are used in salad dressing, mayonnaise, and gravy base.

2.8.4 Freeze-Thaw Properties

When starch gels are subjected to cold storage or freeze-thaw cycling, there is a high tendency for retrogradation (White et al., 1989). It is therefore an important consideration that starch thickened foods withstand these storage conditions. Conditions during cold storage are optimum for promoting retrogradation (Pomeranz, 1985).

Retrogradation during cold storage can easily be determined by measuring the paste reflectance during storage (Schoch and Elder, 1955). Figure 2.6 shows the changes of reflectance as a function of storage time at 4°C, for different starches (Pomeranz, 1985).

Figure 2.6: Change in starch paste reflectance during storage at 4°C.



Freeze-thaw stability of starch pastes is often measured by determining the effect of syneresis on the pastes. Syneresis refers to expulsion of water from starch gels during storage. Freeze thaw stability is then determined by measuring the amount of liquid separated from the starch gels as a function of storage time at a given temperature, or after certain number of freeze thaw cycles (White et al., 1989). Figures 2.7 and 2.8 show cold storage stability and freeze-thaw stability respectively, of various starches as measured by the amount of water separated from the gels during storage (Pomeranz, 1985).

Figure 2.7: Cold storage stability of various starches as measured by water separated from the gel during storage at 5°C (40°F).

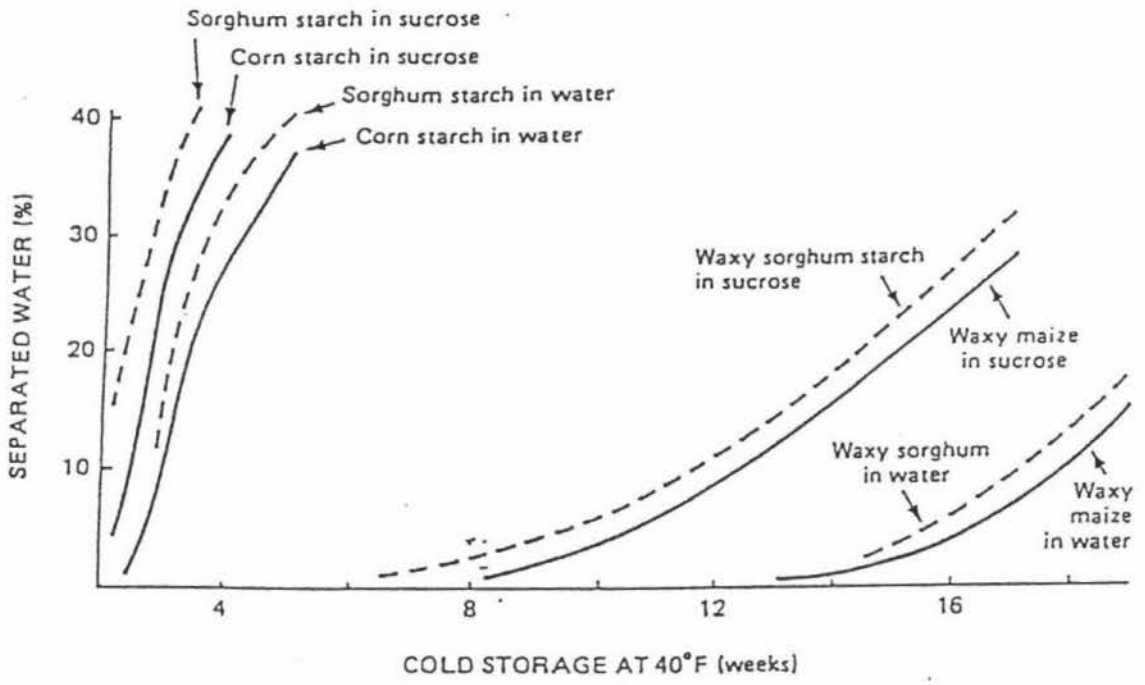
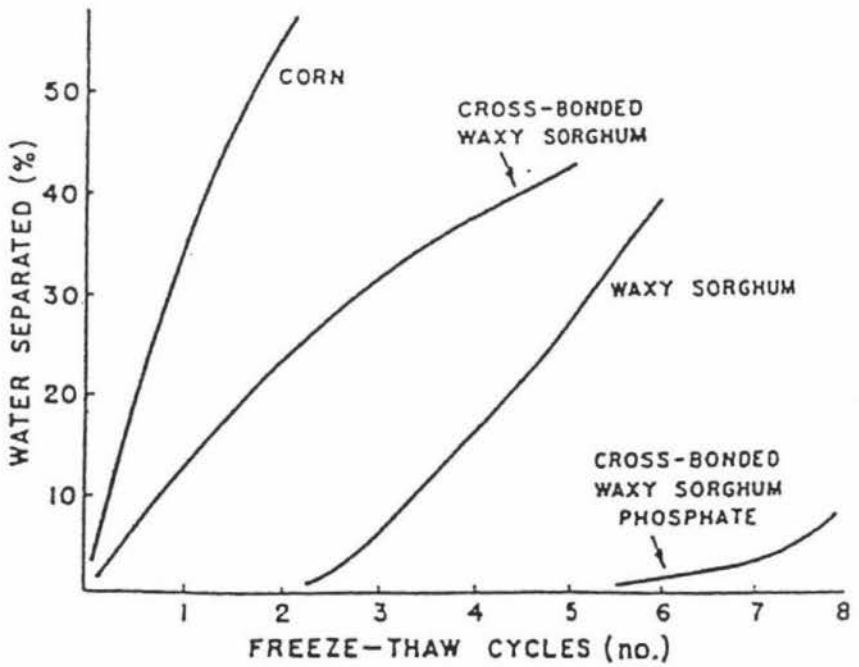


Figure 2.8: Freeze-thaw stability of various starches as measured by water separated from the gel after freeze storage and thawing

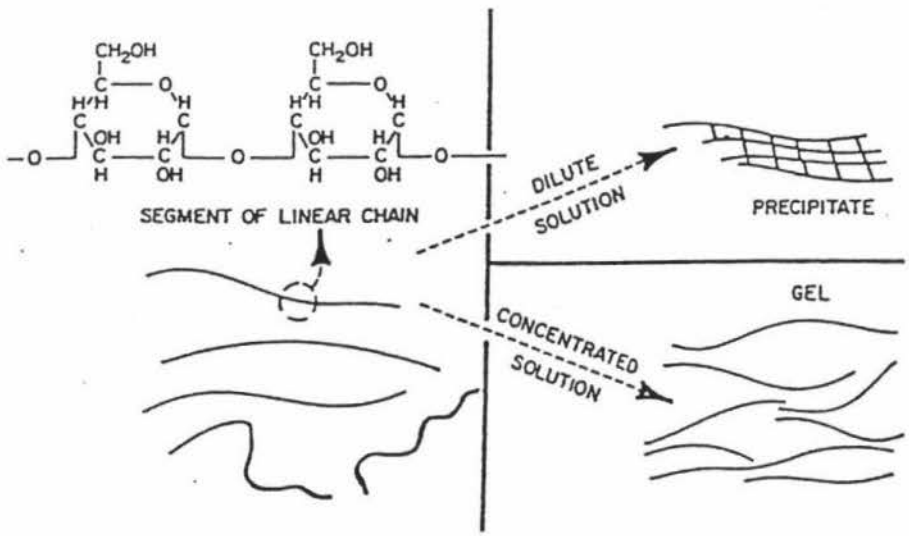


The problem of water separation can be eliminated by introducing ionic phosphate groups into the cross-bonded waxy starch. Mutual repulsion between negatively charged phosphate sites dilates starch molecules and thus maintains the high water holding capacity of the starch-paste. By increasing the amount of phosphate ionic groups, freeze-thaw stability can be increased to any desired degree (Pomeranz, 1985).

2.8.5 Starch Retrogradation

During gelatinization the starch molecules are well dispersed throughout the entire water-starch system. Because of the abundance of hydroxyls, these molecules have high affinity for moisture which gives rise to high dispersibility in water (Wurzburg, 1986). The dispersed molecules, however, may come into contact with each other during storage, forming hydrogen bonds between hydroxyl groups of adjacent polymers. Contacting of molecules may be due to the effect of linearity, mobility and hydroxyl of polymers (Sterling, 1978). The hydrogen bonding will give rise to reorientation and reassociation (often referred to as recrystallisation) of parallel molecules forming insoluble aggregates or precipitates. At higher concentration, steric hindrances interfere with reorientation of polymers thus forming a three-dimensional gel (Wurzburg, 1986). Figure 2.9 diagrammatically shows the formation of precipitates at low starch concentration (Hood,1982).

Figure 2.9: Formation of starch precipitates at low starch concentration



The longer the starch chains the greater the number of hydrogen bonds which will connect them with their neighbours. Amylose molecules are more firmly bonded, than amylopectin, because of their linear structures (Sterling, 1978). Because of this reassociation of molecules, the affinity of the dispersed starch molecules for moisture is reduced and the water molecules are displaced by the starch-starch bonds (Sterling, 1978). The increase in size of the precipitates results in the starch paste becoming opaque. The extent of retrogradation is affected by several factors.

Linearity and length of starch molecules enhance retrogradation. Branch molecules may be more difficult to line up to ease reassociation . Whistler (1953) has reported that there may be an optimum chain length for retrogradation. Small molecules do not associate completely and long molecules may be difficult to line up with their neighbours over long intervals (Sterling, 1978).

Retrogradation is most rapid around the freezing point. Slow removal of water, at this point, to participate in ice crystal formation, leaves naked starch molecules sufficient time to reassociate into aggregates (Sterling, 1978). Retrogradation is hindered at higher temperatures because of the higher kinetic motion of starch molecules and more random reassociation due to this motion (Wurzburg, 1986).

Various modification processes, which provide interference with the reassociation of starch molecules, minimize or eliminate retrogradation in starch-water systems. No information on retrogradation of taro starch gels was found.

2.8.6 Binding and Bulking Properties

The use of starches as binders is very common in non-food industries such as adhesive, textile, and paper industries (Balagopalan et al., 1988). Starches are used as binders in the food industry to a lesser extent. Some meat products such as sausages and canned meat contain significant amounts of non-meat ingredients. These ingredients often include starch which binds meat into a non-crumbly mass and also prevents the mass from drying out too quickly (Knight, 1969). In the case of

canned meat, the purpose of starch is to provide bulk and prevent shrinkage of can contents during the heat treatment. Starches are often used as fillers in many food applications. Starch gives the bulk, replacing some more expensive ingredients such as certain proteins in meat products.

2.9 Concluding Remarks

It can be seen from this review that the functional properties of a starch dictate the way in which that starch is used in industry. These functional properties are revealed by the way in which a given starch undergoes gelatinization and its properties as a gel. These, in turn, depend on various internal granular factors, such as molecular structure and molecular associative forces, and extra granular factors such as the effect of various ingredients and processing conditions.

Application of a starch in industry is determined largely by its ability to retain its desired functional properties during various conditions under which it may be subjected. Determining the suitability, or otherwise, of a starch for a specific application is based on the understanding of its molecular structure, gelatinization and functional properties.

The suitability of taro starch for industrial applications is yet to be determined. There is a lack of information on the functional properties of taro starch, due to insufficient research. As a result, its use in industrial applications is virtually non-existent.

It has been shown also that almost all the information available on taro starch has been on one genus of taro, *Colocasia*. The purpose of this study was, therefore, to study the functional properties of the taro starches obtained from the three most commonly grown taro genera in Tonga.

CHAPTER THREE
MATERIALS AND METHODS

Taro starches were freshly extracted from freshly harvested raw materials. The starches were dried, purified and then used for various investigative studies. In this chapter, the methods used for raw material preparation and measurements are described.

3.1 Raw Material

Taro starches were extracted from three selected cultivars, one from each of the most commonly grown taro genera in Tonga, ie. *Colocasia, Alocasia*, and *Xanthosoma*. The selected cultivars were *Colocasia esculenta* var *'Lau'ila', Alocasia macrorrhiza* var *'Fohenga'*, and *Xanthosoma sagittifolium* var *'Mahele'uli'*. The selected cultivars will be referred to as *Colocasia, Alocasia*, and *Xanthosoma* in the text. These taro genera are briefly discussed below.

Taro *Colocasia esculenta*

Figure 3.1 shows taro *Colocasia* corm (South Pacific Commission, 1985). The corm size ranges from 0.5 kg to 5 kg. Among the cultivars of *Colocasia* growing in Tonga, *'Lau'ila'* is the most popular to local growers because it has relatively high yields, short maturity time (4 months), and no known pests attacking it. As an everyday staple food, it has a texture and flavour that are highly appealing to the taste of most Tongans.

Figure 3.1: Taro *Colocasia* corm (South Pacific Commission, 1985).

Taro *Xanthosoma sagittifolium*

Figure 3.2 shows the *Xanthosoma sagittifolium 'Mahele'uli'* plant. Among the cultivars of *Xanthosoma, 'Mahele'uli'* is most popular because it is considered by the local growers to have a relatively high yield. The cormels are the edible parts, and the main corms are used for planting sets and fed to animals (Bourke, 1982). The cormel size ranges from 0.1 to 2 kg. In Tonga and probably the other Pacific countries, the corms can be peeled, grated and mixed with grated cassava and used in the preparation of various traditional delicacies (Havea, 1992). Many cormels are produced per plant, up to 35, and cormel yields are usually higher than *Colocasia* (Bradbury and Holloway, 1988). The young leaves are used in preparation of various traditional dishes in the Pacific countries.

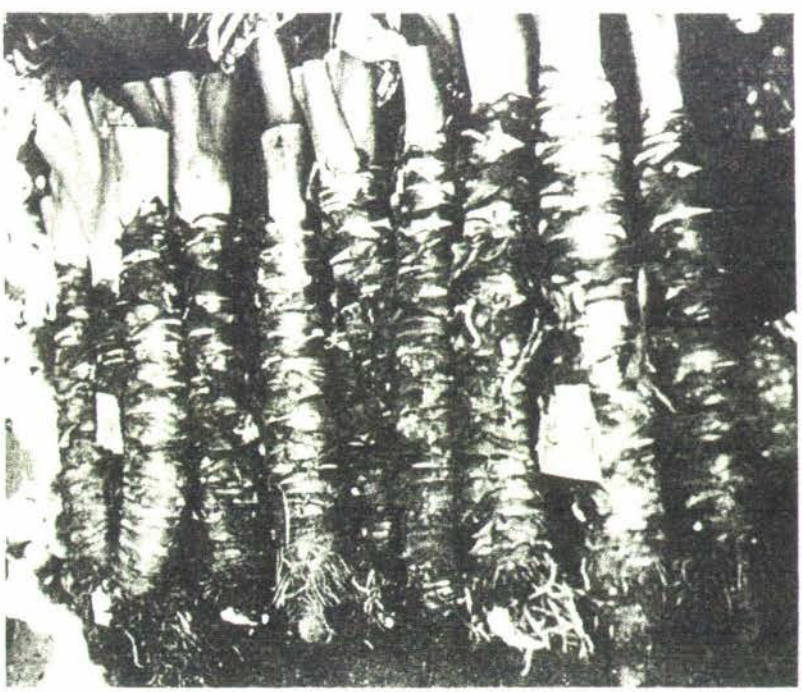
Figure 3.2: Taro *Xanthosoma sagittifolium*

Giant Taro, *Alocasia macrorrhiza*

Giant taro, *Alocasia macrorrhiza* (Figures 3.3 and 3.4), the largest of all the taro cultivars, grows well under evenly distributed high rainfall, since it cannot withstand waterlogged conditions or prolonged drought (Bradbury and Holloway, 1988). The corm grows above the ground as a stem, typically 1 m long, 15-25 cm in diameter and weighs up to 30 kg (Bradbury and Holloway, 1988). Giant taro cultivars are known in Tonga to be more acrid than both *Colocasia* and *Xanthosoma* cultivars. Giant taro grown under poor conditions like poor soil fertility, or prolonged drought condition, often results in high acridity.

Figure 3.3: Giant taro (*Alocasia macrorrhiza* var *'Fohenga'*)

Figure 3.4: Giant taro corms at Apia market (Bradbury and Holloway, 1988).



Only the stem of giant taro is edible in Tonga and the Pacific countries, however, Sakai (1983) has reported that the leaves are also eaten in Indonesia. '*Fohenga*' is a prestigious food in Tonga. It is widely used in feasts and various cultural occasions.

The selection of these cultivars was based on pre-determined factors including: starch content, size of starchy edible parts (corms or cormels), time to maturity, and being commonly grown for commercial purposes in Tonga. The selection process is presented in Appendix 2.

The extraction of starch from taro *Xanthosoma* was carried out in Nuku'alofa, Tonga, from taro *Alocasia* was started in Tonga and completed in New Zealand, from taro *Colocasia* was carried out in New Zealand. The simple starch extraction method used for *Xanthosoma* could not be used for *Alocasia* and *Colocasia*. This was due mainly to the difficulties encountered when trying to separate the starch from the starch milk. Therefore, concentrated starch milk of *Alocasia,* and fresh corms of *Colocasia* were transported to New Zealand, and then the starch extraction was carried out in the pilot plant at the Food Technology Department, Massey University with the incorporation of a bowl centrifuge (MSE 467) in the process. The taro (*Colocasia* corms) were blended using a Kenwood blender, and the extracted starch was dried using a Whitlock hot air tray drier at 40°C for 24 hours.

Cassava (tapioca) starch of commercial grade was obtained from National Starch & Chemical NZ Ltd. Auckland, (a product of Thai-Wah Company Ltd., Bangkok). Tests were carried out for all the taro starches as well as for the cassava starch for comparison.

3.1.1 The Starch Extraction Process

The method used in extracting starch was a modification of the method presented by Agboola et al. (1990) for extraction of starch from cassava. Taro corms or cormels were freshly harvested by the farmers by manually digging from the ground and

transported to the processing site, about 100 to 120 kg of each cultivar. Fresh taro was peeled by hand, washed, weighed, and then ground into taro pulp using a motor driven grinder (Figure 3.5, a home designed grinder). The starch was then extracted through a fine cheese cloth by washing with excess water while mixing the pulp to facilitate the starch slurry passing through the filter cloth, (Figure 3.6). The filtrate was collected in a settling tank where the starch was allowed to settle for 24 hours. The liquid was then discarded, and the solid starch cake was pressed through a fine wire mesh screen to form fine pieces of starch lumps. This was carried out mainly to assist the drying process. The starch was then air-dried at 40°C for 24 hours, using a temporary drier, newly constructed from particle board (Figure 3.7). The dried starch was packed in polyethylene bags and then shipped to New Zealand. Figure 3.8 summarises the starch extraction process.

Figure 3.5: A home designed motor driven grinder

Figure 3.6: Extraction of starch by manual mixing of taro pulp

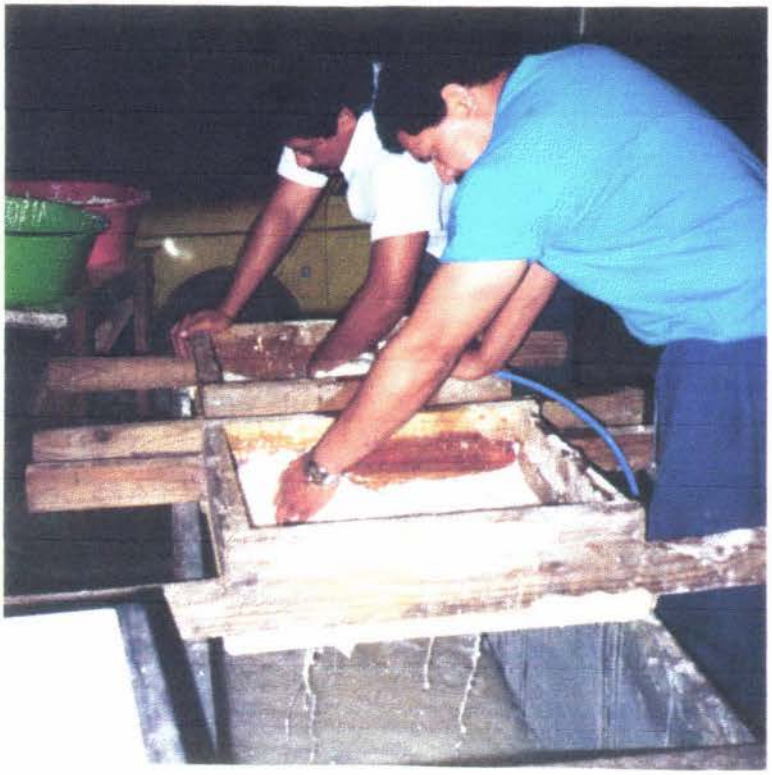
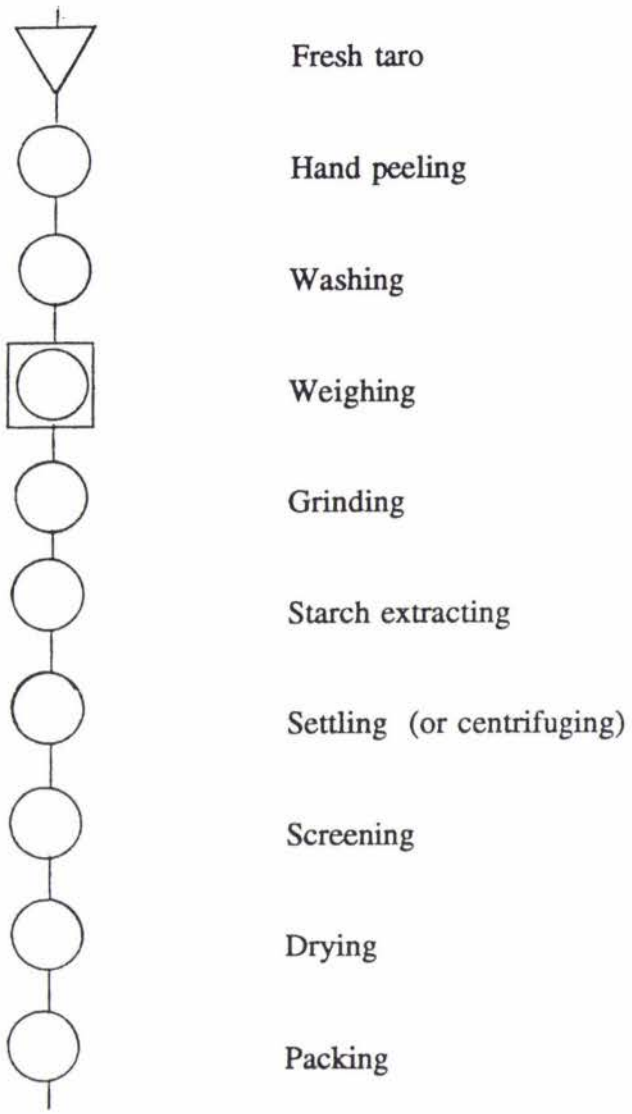


Figure 3.7: A hot-air drier, designed for drying starch

Figure 3.8: Flow chart for starch extraction process



The settling process was used only for separating the starch from the *Xanthosoma* starch milk. For both *Colocasia* and *Alocasia* a bowl centrifuge was used.

3.2 Starch Purification

The raw starches were analyzed for protein, fat and total dietary fibre contents. Protein was determined using the Kjeldahl method for determining the nitrogen content, as described by Smith, 1964. The percentage nitrogen content was multiplied by a conversion factor, 6.25 (Bradbury and Holloway, 1988) to get the

percentage protein content. Fat content was determined using the method of Schoch, 1964. Fibre content was determined using the method of Horwitz, 1980.

The method employed in purifying the starches was that of Badenhuizen, 1964; and modified by Adkins et al., 1966. The starch sample was suspended in an equal amount of distilled water, and then gently shaken and centrifuged at 1500 G in 250 ml centrifugal bottles for a few seconds, then the liquid phase was discarded. This washing process was repeated four times.

This washing process was to remove all residual impurities from the starch. It should also have removed the raphide crystals. Wang (1983) reported that raphide crystals can easily be washed off from the taro flesh during cutting, washing and processing of taro.

The starch was then resedimented in 0.1 M sodium chloride solution. The saline suspension was then shaken with toluene (0.1 volume) for four hours. The protein-toluene layer was then discarded. The starch sample was then refluxed with 80% aqueous methanol for twelve hours. It was washed with acetone and then ether. The sample was washed with water four times and then stored at 4°C under toluene. The starch was washed with distilled water several times before using.

3.3 Starch Granules: Morphological and Molecular Structure

The granule physical characteristics, size and shape, of the taro starches were studied, in comparison to that of cassava starch. To describe the molecular characteristics of the starches, the amylose contents of the starches were determined.

3.3.1 Morphological Structure

For each starch sample, a 10 ml, 2% w/w starch slurry, was prepared by mixing 0.2g. (dry weight) of starch in 9.8 g of distilled water. A drop of each starch slurry was placed on a microscope slide, covered with a cover slip and studied under a Nikon

Alphaphot-2 YS2 light microscope. The granule shape was described and the actual granule size range of each starch was measured using an Olympus Objective Micrometer.

The prepared slide was also used to take photomicrographs of the starch granules. The slide was viewed under an Olympus Photomax 200152 microscope set, upon which a camera had been mounted, and photographs of certain fields, clearly showing features of the granules, were taken for each starch sample.

3.3.2 Molecular Structure

The starch samples were analyzed for amylose content. The amylose contents of the starches were determined using the blue value colorimetry method as described by Morrison and Laignelet, (1983).

3.4 Starch Gelatinization

Starch gelatinization was studied using five different methods: sensory evaluation, hot stage microscope, Brabender Amylograph, DSC (Differential Scanning Calorimetry), and swelling power.

3.4.1 Sensory Evaluation Method

In the sensory evaluation method, a gel was prepared from each starch sample by heating a 7% w/w starch suspension (7 g starch, dry weight, suspended in 93 g distilled water) in a beaker, using a bunsen burner while stirring continuously using a glass rod. A glass thermometer was used to measure the temperature of the suspension during the heating process. The gelatinization temperature was recorded as the temperature (range) at which the starch suspension started to lose opacity and became clear, and an apparent increase in viscosity was observed. This method of gelatinizing the starch suspension was used only in the early part of the

experimentation, since it was primarily to obtain quick results that provided ideas on the gelatinization temperatures of the starches. Three samples of each starch were heated, and the gelatinization temperature was the average of those recorded temperatures.

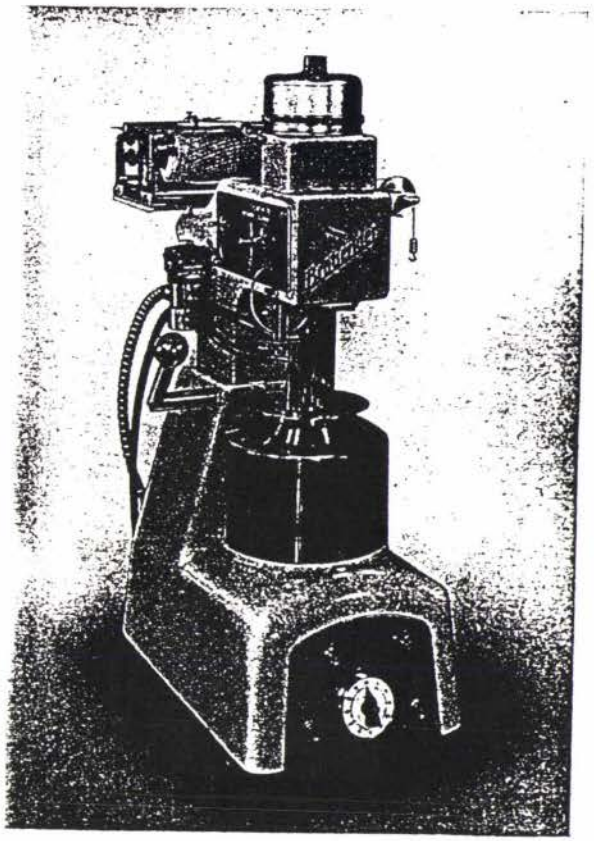
3.4.2 Hot Stage Microscope Method

In hot stage microscope (Leitz Wetzlar, Sofi 6920) method, a 2% w/w starch-water suspension was prepared for each starch sample. A drop of each suspension was mounted on a microscope slide, covered with a cover slip, and placed on the stage. The stage was then heated at a constant rate, 2.5°C per min. The starch was observed closely for the onset of gelatinization, as being the "bursting" or "disappearing" of individual granules. The gelatinization temperature range, was recorded as the temperature at which the granules started to "burst" until, almost 80% of the granules had been "burst". At least three measurements of each starch sample were made.

3.4.3 Brabender Amylograph

A Brabender Amylograph Type VS 6S 3031 (Figure 3.9) was also used to measure the gelatinization of the starches. A 10% starch slurry, 500 ml, of each sample was prepared by suspending the appropriate amount of starch in distilled water. The slurry was then transferred to the measuring cup and heated at a rate of 1.5 °C/min. The amylograph continuously measured and recorded the viscosity and produced the pasting amylogram of each starch sample. The measurement was carried out over the following stages: heating from 30°C to 95°C at 1.5 °C/min, holding at 95°C for 5 minutes, cooling from 95°C to 50°C, at -1.5 °C/min.

Figure 3.9: Brabender Amylograph



3.4.4 Differential Scanning Calorimetry (DSC) Method

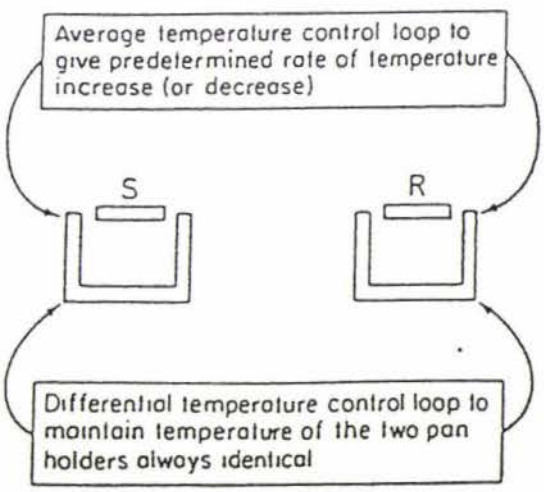
Heat is either absorbed or liberated when a material is undergoing a change in physical state (eg. melting, evaporation or chemical reaction). The DSC is designed to determine the enthalpy of these processes by measuring the differential heat flow required to maintain a sample of the material and an inert reference at the same temperature. This temperature is usually programmed to scan a temperature range by increasing linearly at a predetermined rate (McNaughton and Mortimer, 1975).

The purpose of differential thermal systems is to record the difference between the enthalpy change which occurs in a sample and that in some inert reference material, when they are both heated. These systems may be classified into three types (Perkin-Elmer Corporation, 1970): 1. Classical DTA (Differential Thermal Analysis); 2. 'Boersma' DTA; and 3. Differential Scanning Calorimetry (DSC). Detailed review

on the theory, operation, and applications of these systems can be found in McNaughton and Mortimer (1975). Details of the theory and design of DSCs have been given by Watson et al., (1964).

In the DSC systems, the sample and the reference are each provided with individual heaters. This makes it possible to use a 'null-balance' principle. It is convenient to think of the system as divided into two control loops as shown in Figure 3.10 (McNaughton and Mortimer, 1975). One is for temperature control, so that the temperature of the sample and reference may be increased at a predetermined rate, which is recorded. The second loop ensures that if a temperature difference develops between the sample and reference, because of exothermic or endothermic reaction in the sample, the power input is adjusted to remove this difference. This is the null-balance principle. Thus, the temperature of the sample holder is always kept the same as that of the reference holder by continuous and automatic adjustment of the heater power. A signal proportional to the difference between the heat input to the sample and that to the reference, dH/dt, is fed into a recorder (McNaughton and Mortimer, 1975).

Figure 3.10: DSC system showing the control system



The gelatinization characteristics (onset temperature T_o, peak temperature T_p, and enthalpy, ΔH) of the test starches were studied using a Perkin-Elmer DSC-7, equipped with a Thermal Analysis Data Station. Benzoic acid, with a known melting

temperature and enthalpy of 395.6 K and 147.2 J/g respectively (Mackenzie, 1970) was used to calibrate the DSC, and the temperature was adjusted to within ±0.05 K, and the enthalpy was adjusted to within ±0.05 J/g.

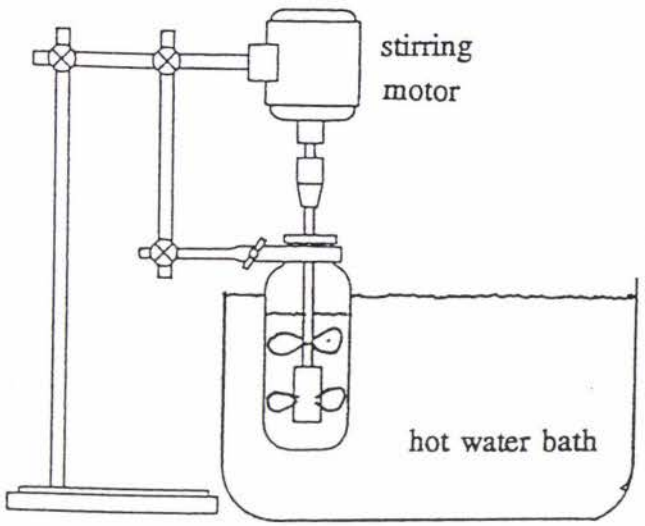
Starch-water suspensions, 7%, 10%, 20%, and 30% w/w, were prepared for each starch. These concentrations were arbitrarily chosen to be used in this study in order to see the effect of different concentrations on the gelatinization. About 50 to 95 mg samples of those starch suspensions were accurately weighed and hermetically sealed in Large Volume SS Pans, PE No. 0319-0021. The samples were left at room temperature for two hours to equilibrate before DSC measurements were made.

Before each measurement, the sealed sample was placed in a small plastic test tube and then shaken for five seconds using a vortex test tube shaker. Each sample was then analyzed by placing it in the analyzer, and then scanning at a predefined rate of 20 °C/min over the temperature range of 25 to 120°C. The enthalpy of gelatinization (ΔH), the gelatinization onset temperature (T_o) and the peak temperature (T_p) were computed automatically by the analyzer.

3.4.5 Swelling Power

The swelling power of the granular starches were determined following the method of Schoch, 1964. About 1 g, dry basis, of starch was accurately weighed into a 250-ml centrifuge bottle. 200 g of distilled water was added. The bottle and a stirring motor were arranged in position (Figure 3.11) on a vertical metal rod, which in turn was attached to a support stand by a single clamp. This arrangement was used to hold the bottle down in a hot water bath which was thermostatically maintained at 85.0°C ± 0.2°C.

Figure 3.11: Apparatus for swelling power determination



This heating was carried out for 30 mins. while stirring continuously. The paste was then centrifuged at 2200 rpm for 15 minutes. The supernatant was drawn off by means of a glass tube attached to a suction flask. A 50 ml aliquot of this solution was transferred to a tared nickel evaporator dish and evaporated to dryness in a 105°C hot air oven. The bottle and the content were weighed on a torsion balance to give the weight of the swollen starch granules. A correction was made for soluble starch, in order to provide a measure of swelling of the swollen but undissolved granules. This was carried out by multiplying the percent solubles by a factor of 4 (Schoch, 1964). The following calculations were employed:

$$\text{\% Solubles (on dry basis)} = \frac{\text{Weight of soluble starch} \times 4 \times 100}{\text{Weight of sample on dry basis}}$$

$$\text{Swelling power (corrected)} = \frac{\text{Weight of sedimented paste} \times 100}{\text{Weight of sample on dry basis} \times (100 - \text{\% Soluble, dry basis})}$$

Duplicates of each sample were analyzed, the swelling power was recorded as the average of the two calculated values.

3.5 Functional Properties of Starch Gels

Gels of starch samples were prepared using the standard method described below. These gels were used to investigate various gel functional properties. This section describes the methods used for these investigations.

3.5.1 Gel Preparation

Because there were several required investigations into different properties of the starch gels, it was decided that a standard gel preparation method be used. The following method was therefore used in preparing all gels used in this study.

The slurry was prepared by suspending and mixing a calculated weight of starch (dry weight) and distilled water to obtain the desired concentration. The slurry was placed in a plastic container and arranged in a vertical position with an electric stirrer, the same arrangement as that shown in Figure 3.11 above (Section 3.4.5). The container lid had a hole with a size that allowed free rotation of the stirrer, while minimizing the evaporation of water during heating. The container and the stirrer were clamped to a supporting steel rod. This set was arranged so that the level of the slurry in the container was fully emerged in a hot water bath kept at 90 - 95°C, by a thermostat controller. With continuous stirring at 200 rpm, the starch slurry was allowed to gelatinize for 45 minutes. The arrangement was then removed from the water bath, the stirrer was removed from the container, and the gel was ready to be used for further tests.

3.5.2 Gel Strength

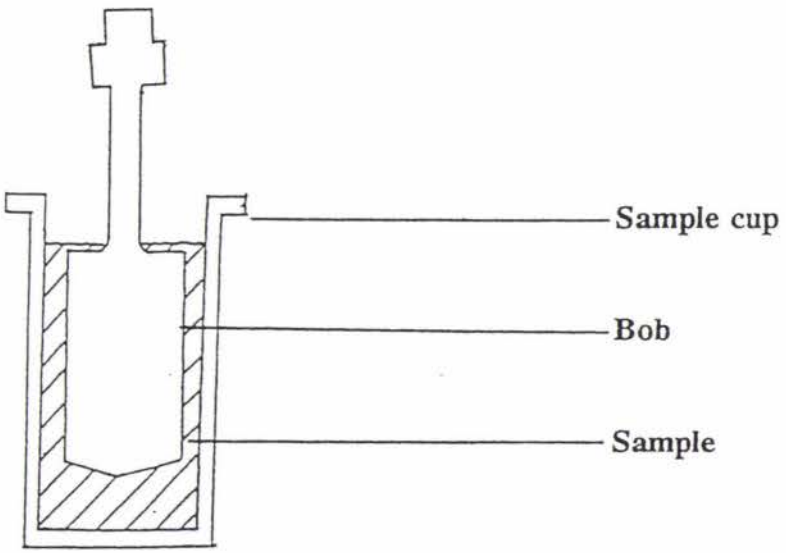
The gel strength was investigated using two main methods: rheological measurement using a Bohlin VOR Rheometer, and tensile and compressive strength measurement using an Instron. These methods are described in more detail below.

Rheological Measurement

- Theory

The C25 measuring system (Figure 3.12) consists of a fixed bob (inner cylinder) and a rotating cup (outer cylinder) with the sample contained in the annular gap between them.

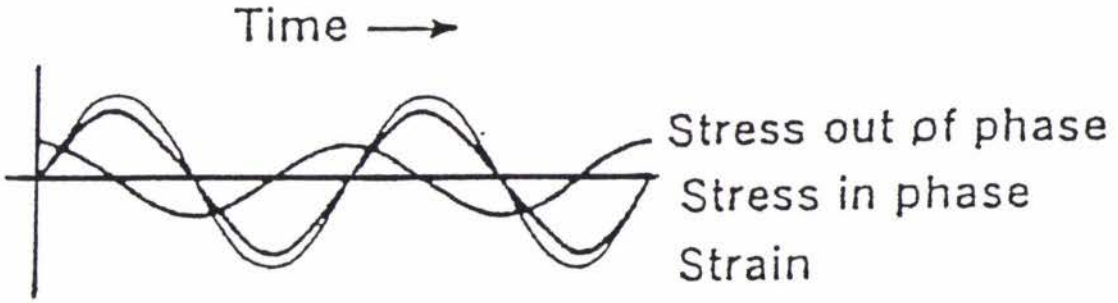
Figure 3.12: C25 Measuring System of the VOR Bohlin Rheometer



During measurement in the oscillatory mode, the cup oscillates applying a sinusoidal deformation of defined amplitude (γ_o) and frequency (0.9 Hz for this particular test). The material applies a resistive torque which is measured by the measuring device, converted to shear stress, of amplitude τ_o, and recorded by the computer data station.

The principles underlying this measurement are described as follows. When a linear viscoelastic body is subjected to a strain varying sinusoidally with time, (ie. when the cup oscillates), its mechanical behaviour at a single frequency can be specified by two rheological parameters: the strain applied and the stress which is generally not in phase with the strain (Figure 3.13).

Figure 3.13: Two components of deformation stress



The out-of-phase angle, referred to as the phase angle (δ), depends on the nature of the viscoelastic material. A viscoelastic material can be viewed as having a solid and a liquid components. For a perfect solid, the phase angle is equal to zero ($\delta = 0$), and for a perfect liquid, the phase angle is equal to 90 degree ($\delta = 90$). For a viscoelastic material, the phase angle is somewhere between zero and ninety degree ($0 \leq \delta \leq 90$).

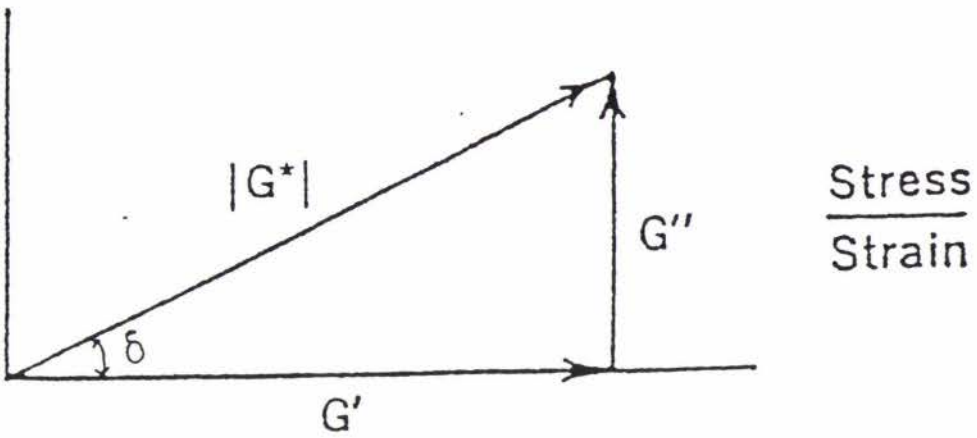
Knowing the strain and the resulting stress due to oscillatory motion three different moduli can be defined. The storage modulus G', which can be interpreted as the solid component of the gel, is the component in phase divided by the strain. The loss modulus G", which can be interpreted as the liquid component of the gel (also referred to as the imaginary part of the material), is the 90 degree out-of-phase stress component divided by the strain. The complex modulus G*, which to a certain degree could represent the gel strength, therefore, describes the resulting contributions of these components that give rise to the viscoelastic nature of the material, $G^* = G' + iG''$. The relationship between these moduli can be viewed vectorially, as shown in Figure 3.14.

$G' = \tau_0/\gamma_0 \cdot \sin \delta$ (storage modulus)

$G'' = \tau_0/\gamma_0 \cdot \cos \delta$ (loss modulus)

$G^* = \sqrt{(G'^2 + G''^2)}$ (complex modulus - "gel strength")

Figure 3.14: Relationship between G*, G' and G" moduli



During measurement the machine actually records all the parameters related to the rheology of the gel. These include G', G", G*, δ, time, temperature, viscosity, frequency, range, amplitude, and a correction factor. These parameters are plotted automatically in a graph during each run. A typical table of recorded data and plotted graph is given in Appendix 3 A & B.

The frequency (0.9 Hz, to compare data obtained by Eliasson and Kim, 1992) and amplitude (5%) were defined in this study. The correction factor was a measure of the degree to which the measuring device was automatically adjusted to ensure the measurements followed the predetermined conditions. It was kept to a minimum. In all the measurements in this study, the correction factor was between the range of 0.000 to 0.150, which is a very acceptable range.

Starch gels of 5% concentration were prepared using the standard method (Section 3.5.1). The gels were left at room temperature (20°C) for three hours before the rheological measurement was carried out.

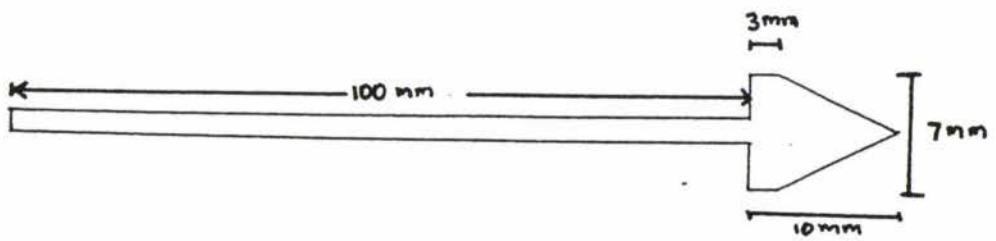
The rheological measurement was carried out following the method of Eliasson and Kim (1992). The changes in the rheological parameters: complex (G*), storage (G'), and loss (G") moduli, viscosity (η), and phase angle (δ), of the prepared gels were followed in the oscillation mode in a Bohlin VOR Rheometer. The C-25 conical

cylinder measuring system was used. A 40 gcm^{-2} torque bar was used. Fifteen ml of each starch gel was transferred into the sample cell of the rheometer and the cylinder was slowly lowered to a cap of 4.5 mm from the bottom. A thin layer of paraffin oil was added on top of the gel to avoid water evaporation during measurements. The initial equilibrium time was 120 s. The sample was then heated from 25 to 90°C at a rate of 3 °C/min, and the dynamic rheological parameters were continually monitored every 30 s.

Instron Measurement

The gels were tested for penetration strength using an Instron (Model No. 4502, S. No. H3096). A 10% starch gel of each sample was prepared using the standard method. The gels were transferred into cylindrical plastic containers of dimensions, 25 mm i.d. and 70 mm height. The gels were filled to a depth of 5 cm, centrifuged at 2200 rpm for 10 seconds to remove air bubbles, and then left at room temperature for two hours, before measurements were carried out. A 10 N load cell, and a cone shaped device (Figure 3.15) was used to penetrate the gel to a depth of 3 cm at a rate of 5 mms^{-1}, while the penetrating force was continuously monitored by a computer data recorder. Three replicates of each sample were tested and the average of the three were taken to represent each starch gel.

Figure 3.15: The cone shaped device used for Instron penetration of the starch gels



3.5.3 Gel Clarity and Texture

Gel clarity and texture were assessed by sensory evaluation. The gels prepared as described in Section 3.5.1 were evaluated qualitatively for gel clarity and elasticity of texture. This was carried out by three post graduate Food Technology students

in a form of group discussions. Each student was asked to put the gels in order of clarity, from highest to lowest clarity. Using a stirring rod to stir and evaluate the gel structure, each gel was compared in terms of its clarity and elasticity compared with cassava starch gel which was used as reference starch. This evaluation was carried out on the gels immediately after preparation.

3.5.4 Crystallization

The crystallization of taro starch gels during storage was also studied. This was carried out using DSC, following the method of White et al., 1989. Starch slurries of (starch/water) 7%, 10%, 20%, and 30% concentrations of each test starch were prepared as in Section 3.5.1 and used to prepare samples for DSC measurements. Fourteen samples of each starch and concentration were prepared and scanned in the same way and conditions as described in Section 3.4.4 above. Each set of samples was then halved and stored in 5 and 22°C for ten days before they were rescanned again in the same way and conditions as previously described in Section 3.4.4. The crystallisation of starch gels was calculated as the ratio of the enthalpy of gel crystallisation after storage (ΔH_s) to the enthalpy of gelatinization (ΔH_g) of raw starch slurry expressed as percentage.

$$\% \text{ Crystallization} = \frac{\Delta H_s \times 100}{\Delta H_g}$$

3.5.5 Development of Opacity

Development of opacity in starch gels during stotage were observed qualitatively by using glass test tubes. A 5% w/w gel of each starch was prepared using the method described in Section 3.5.1. The gels were transferred to glass test tubes. Duplicate test tubes of each gel were stored at 5 and 30°C for 10 days. Photographs of the gels were taken before and after storage.

3.5.6 Syneresis

Taro starch gels were investigated for their tendency to undergo syneresis at various storage temperatures. A 5% starch gel of each starch was prepared and then transferred to 15 ml pre-weighed centrifugal tubes, and weighed to get the total weight of the gel sample. Eighteen tubes of each starch gel were stored at 5, 22, and 30°C. Three samples of each set of tubes were taken after storage for 24 hour, 2 day, 4 day, 8 day, and 12 day storage periods for syneresis testing. These samples were centrifuged at 2200 rpm for 20 minutes, the separated water layer was then discarded and the tubes were reweighed to get the weight of of water separated. The weight of liquid separated was measured and the extent of syneresis was expressed as the percentage of liquid separated per total weight of sample in the centrifuge tube.

$$\text{Syneresis (\%)} = \frac{\text{liquid separated (g)} \times 100}{\text{total weight of sample (g)}}$$

The average of the three samples for each set was then calculated.

3.6 Freeze-thaw Stability of Taro Starch Gels

The freeze-thaw stability of the starch gels was investigated in terms of their thermoproperties (ie. rheological changes during heating over a temperature gradient) using a Bohlin VOR Rheometer, gel strength as measured by the Instron for their tensile and compressive strengths, crystallization as measured by the DSC, and syneresis.

3.6.1 Thermoproperties

Gels of 5% starch slurries were prepared. 15 ml aliquots of the gels were transferred to cylindrical plastic containers of almost the same diameter (27 mm) as the inside diameter (27.5 mm) of the concentric cylinders of the C-25 measuring system.

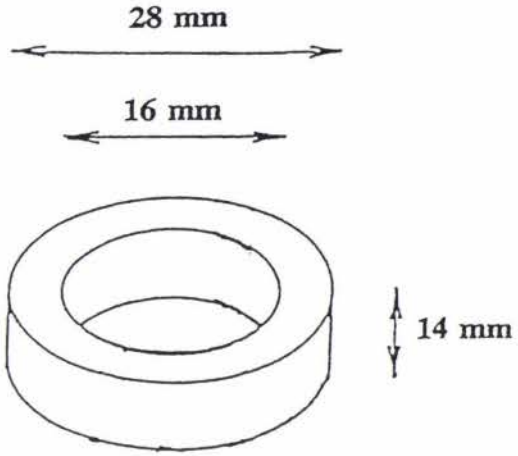
Sixteen samples were prepared for each starch. The samples were then centrifuged at 2200 rpm to remove gas bubbles from the samples. After an equilibration time of two hours at room temperature, a duplicate of each set of sixteen samples were taken for rheological measurement. Four samples from each set were frozen at -10°C, and two of those were taken after 4 days and 8 days storage at -10°C, thawed at room temperature for 5 hours and then used for rheological measurement.

The rest of the samples were then subjected to repeated FT (freeze-thaw) cycles. One FT cycle involved freezing the samples at -10°C for 24 hrs and thawing for 5 hours at room temperature, 20°C. At the end of each cycle, a duplicate of each set of samples were taken for rheological measurements. All rheological measurements were carried out in the same way and conditions as described in Section 3.5.2 above. When the water was squeezed out during setting up the sample for measurement (ie. when the measuring bob was lowered, water might be squeezed out of the gel sample), the sample was not used for rheological measurement, and the trial ceased for that particular starch gel.

3.6.2 Tensile and Penetration Strengths of Starch Gels

For penetration strength of the gels, 10% starch gel of each starch was prepared in the standard way. Twenty samples of each gel were prepared. The samples were centrifuged at 2200 rpm to remove gas bubbles. After equilibration time of two hours at room temperature, two samples from each set were used for penetration strength measurements using the Instron. Six samples from each set were frozen at -10°C, and three of those were taken after 3 days and 6 days storage periods, thawed at room temperature and used for penetration strength measurement. The rest were subjected to repeated FT cycles. FT cycle conditions were the same as those described in the previous section. Three samples from each set were taken at the end of each cycle and used for penetration measurement. Penetration measurements were carried out using the same device, parameters, and conditions as that described in Section 3.5.2 for Instron measurement.

Figure 3.16: Dimensions of gel rings for tensile strength testing using the Instron



For tensile strength measurement, the prepared gel (10%) of each starch was transferred to ring moulds, with dimensions shown in Figure 3.16. The excess gel on top of the mould frame was removed, leaving the surface of the gel parallel to the surface of the mould frame. Fifteen gel rings of each starch were prepared, and after two hour equilibrium time at room temperature the frames with gel were subjected to repeat FT cycles. The conditions for an FT cycle were the same as those previously described. At the end of each cycle, three samples from each set were taken for tensile strength measurement.

The gel rings were removed from the mould. Each ring was hung on L-shaped steel bars of 7 mm diameter arranged vertically. It was then elongated vertically by the Instron at a rate of 3 mm/sec until it fractured. The breaking stress was recorded by the computer data station attached to the instron.

3.6.3 Syneresis

A 5% gel of each starch was prepared using the standard method. Eighteen samples of each gel were prepared using the same method as described in Section 3.5.1. Six samples from each set were frozen and stored at -10°C for 4 day and 8 day periods. At the end of each period, three samples were removed, thawed, and tested for syneresis using the method described in Section 3.5.6. The rest of the samples were

subjected to repeated freeze-thaw cycles, up to five cycles. At the end of each cycle, three samples were removed from each set and tested for syneresis.

3.6.4 Crystallization

A 7% slurry was prepared from each starch. Fifteen DSC samples were prepared and scanned in the same way and conditions as described in Section 3.4.4. The samples were subjected to repeated freeze-thaw (FT) cycles. At the end of each cycle, three samples were taken from each set of fifteen, and then scanned in the DSC in the same way and conditions as described above in Section 3.4.4. The rest were then returned to the freezer and stored for another freeze-thaw cycle. The same set of data, T_o, T_p, and ΔH, were recorded for each sample. The trial went on to five cycles. The ΔH after each FT cycle was a measure of crystallization of the starch molecules at the end of FT treatment.

CHAPTER FOUR
STARCH EXTRACTION AND PURIFICATION

4.1 Introduction

There was no available commercial supply of taro starch. The taro starch was therefore extracted from fresh samples. The starch extraction was carried out in Nuku'alofa, Tonga. Freshly harvested taro was manually peeled, washed, and then ground into taro pulp using a motor driven grinder. The starch was extracted from the pulp, dried in a hot air drier at 40°C for 24 hours. The dried starch was stored in air-sealed containers in a cool room, 10°C, and was purified before being used for subsequent analyses. In this chapter, the extraction, purification processes, and results are discussed in more detail.

4.2 The Starch Extraction Method

Cassava starch is one of the most commonly used industrial tuber starch. Extraction of cassava starch involves the conventional settling method (Agboola et al., 1990). This method can be successfully employed in cassava starch extraction because cassava contains 80% of starch on a dry basis, little protein, fibre or other polysaccharides (Moorthy, 1991). As a result the starch settles fast and can be easily obtained in a pure white form.

Unfortunately, settling of other tuber starches faces some degree of difficulty. In the case of taro, the starch does not settle quickly due to the presence of mucilaginous material (Moorthy, 1991). The starch therefore takes a long time to settle, which can result in microbial contamination and often very low yields.

Moorthy (1991) demonstrated a new method for extracting tuber starches other than cassava in which a 0.03 M ammonia solution was used instead of water. For *Colocasia* extracted using 0.03 M ammonia, a 6-16% improvement in the yields was achieved, the total amylose was unaffected, the peak viscosity was largely increased,

and the swelling volume was enhanced by 25%. This method is only suitable for laboratory applications. For industrial applications it may not be suitable since it alters the functional properties of the starch.

A suitable starch extraction method for taro would have to overcome the problem of the presence of the mucilaginous material without altering the functional properties. In industrial manufacturing of taro starch, it might be more appropriate to employ the available technologies such as centrifugation, as in the industrial manufacturing of cassava starch (Knight, 1969).

An attempt was made to develop an extraction method for taro starch (Section 3.1.1). Moorthy's method was used for *Colocasia* cultivars only. The method developed in this study was used for extracting starch from all the selected taro cultivars.

4.2.1 Raw Materials

Studies on taro starch have shown that there are reasonable variations in properties of starch among the same cultivars growing in different locations, (Moorthy et al., 1993), and stages of growth, (Sugimoto et al., 1987). To minimise the effects of these variations, each taro sample was obtained from one farmer. The *Xanthosoma* sample was bought from a farmer from the Hihifo district (Houma, Tongatapu). It was harvested (pulled and dug out of the ground), and transported to the processing site on the same day. The *Alocasia* sample was bought from a farmer from the Vava'u district (Longomapu). It was harvested and shipped to the main island, Tongatapu, arriving one day after harvesting. The *Colocasia* sample was bought from a farmer from 'Eua district and was shipped to Nuku'alofa and transported to the processing site on the same day of harvesting. Each sample was processed the following day after arriving at the processing site. Because of unsuccessful attempts to extract starch from *Colocasia*, a second sample was obtained from the same farm and location as the first *Colocasia* sample. This sample, however, was shipped to New Zealand and was processed three days after harvesting.

There has been no reports on the effect of raw material freshness on the functional properties of the extracted starch. The raw materials used in this study were relatively fresh. The variations in the starch functional properties over the 1 to 3 day storage before processing was considered minimal. There were virtually no physical changes of the raw taro samples observed during this storage period.

It was most likely that each farmer had planted a taro plantation all in a single day, ie. each taro sample was the same in terms of maturity. Because the raw materials were obtained from the local domestic farmers in Tonga, there was no record of the exact maturity of each taro sample. However, the farmers could provide the month in which each plantation was planted. Table 4.1 presents the characteristics of the raw materials.

Table 4.1: Raw material and starch extraction results

Characteristics	Alocasia	Colocasia	Xanthosoma
Maturity	12 months	6 months	8 months
Month planted	August 1992	Feb 1993	Dec 1992
Date harvested	22 Aug. 1993	27 Aug. 1993	11 Aug. 1993
Date of processing	24 Aug. 1993	31 Aug. 1993	12 Aug 1993
Edible starchy part	corm (stem)	corm	cormels
Peeled size (smallest-largest)	5-15 kg	1.2-3.8 kg	0.4-1.5 kg
Weight of raw materials	106 kg	98 kg	102 kg
Average cost	$1/kg	$1.20/kg	$0.85/kg
Extractability[a]	poor	very poor	very good
Raw starch extracted (Wt. after drying)	16 kg	14.3 kg	22 kg
Moisture[b] of dried starch (%)	16	17.4	13.5

a: Ease of separation, and settling of starch.

b: Moisture contents determined by drying pre-weighed starch samples overnight in hot air oven and determining the moisture loss.

Maturity of raw material was a very important factor in obtaining the optimum yields. Wills et al. (1983), reported that the starch content of taro *Colocasia* increased with maturity. Bradbury and Holloway (1988) reported that the starch content of various cultivars of taro decreased with exceeding maturity (eg. more than 12 months for most *Colocasia* cultivars) due to biosynthetic changes that result in increase of moisture content.

The *Alocasia* sample can be considered to be fairly young, since the plant can be grown for up to a few years. However, the size of the corms, edible starchy part, as seen in the table, was relatively large. The *Colocasia* and *Xanthosoma* samples would have been in full maturity. Most growers in Tonga would harvest these cultivars at about this maturity time. *Colocasia* can be left unharvested for a few more months while for the *Xanthosoma* cultivar, the cormels (edible starchy part) can undergo a rottening effect, particularly if it is raining season, (a comment by one of the local growers).

There was no problem with the availability of the raw materials in Tonga, during the time of the trip, August. However, the costs of taro were considered to be very high. Interviewing several growers showed that there was a short supply of taro, at the time of the trip due to shifting of domestic farmers to commercial growing/exporting of squash pumpkin to Japan. Exportation of squash pumpkin to Japan is currently a very successful and attractive project and has taken away the growers from traditional domestic farming of staple food crops such as cassava, banana, and taro. Normally, taro would not cost this much.

4.2.2 The Processing

The use of the conventional settling method in separating starch from the starch milk worked only for *Xanthosoma* starch. After extracting the starch from the pulp, the *Xanthosoma* starch settled very quickly to the bottom of the settling tank, very much the same as settling of the cassava starch. It took only a few hours (3-5), for a solid

starch cake to form at the bottom of the tank, leaving a relatively clear supernatant on top, which was easily discarded.

In the cases of *Alocasia* and *Colocasia*, it was found that the use of this conventional settling method was unsuitable to separate starch from the starch milk of both of these cultivars. This was mainly due to poor settling of starch in the starch milk. The starch failed to form a separable solid cake at the bottom of the settling tank. This resulted in transportation of the raw material, raw taro corms for *Colocasia* and thick starch slurry for *Alocasia*, to New Zealand and the starch extraction process was completed at Massey University. The separation of starch from the milk was carried out using a bowl centrifuge (MSE 467).

4.2.3 Transport of Raw Materials to New Zealand

The dried *Xanthosoma* starch was packed in a polyethylene bag, and then sealed in an air-sealed bucket. The raw taro *Colocasia* corms (98 kg) were packed in thick card-board boxes. The raw *Alocasia* starch slurry was packed in air sealed buckets. All these containers were kept in cold store (5°C) during shipment, air freighted, to New Zealand. In the case of *Alocasia* starch, the extraction process was started in Tonga, and the separation of starch from the slurry was completed in New Zealand, three days later. The storage of the starch milk for this period might have some effect on the functional properties of the starch. The main concern was the possibility of enzyme degradation of the starch granules. The effect of enzyme degradation was minimized by keeping the starch slurry in cold storage (5°C) during this delay.

4.2.4 Starch Purification

The purification of starch was carried out at the Food Chemistry Laboratory, Department of Food Technology, Massey University. All the solutions and the solvents used were of analytical (Analar) grade.

The purification of starch involved washing of the extracted starch to remove all impurities. In most starches, the impurities that are of concern to the scientists are mainly fat and protein, which are often associated with the extracted starch and also often affect the functional properties. Both of these molecules have been reported to affect the gelatinization (Miller et al., 1973; Lund, 1984; Light, 1990). In taro starch, the impurities present would be protein, fat, fibre and raphide crystals. Protein and fibre would be the main concern. Fat would not be a major concern, since it is present in very small amounts (< 0.5%, dry basis) in taro tubers (Onwueme, 1978; Standal, 1982; Parkinson, 1984; Bradbury and Holloway, 1988). There is no report on how the presence of the raphide crystals (calcium oxalates), affects the functional properties of the starch. However, it would be easy to remove the raphide crystal during the purification process. It was assumed that they had been removed in the washing process used. This was evident in the microscopic study of the starch granule structure (Chapter 5). There was no crystals observed in any of the taro starches.

4.3 The Extraction Process

4.3.1 The peeling of Taro

The peeling of raw material was done manually. The industrial use of manual peeling has been successfully utilized in Tonga for many years in desiccated coconut processing. After deshelling the coconut, the skin of the coconut meat was then peeled manually. This was fairly economical mainly because of the availability of very cheap labour in the country. The cheap labour (average labour cost, TOP$8-12/day) is currently a resource that could be utilized in industrial processing such as peeling of taro for commercial starch extraction.

Other industrial peeling methods could also be used. Abrasive peeling could be used for both *Xanthosoma* and *Colocasia*. This however, cannot be used for *Alocasia* since there is a need for a complete removal of the highly acrid thick skin. A high

pressured hot water blasting might be another method that can be used. These methods, however, were not attempted in this study.

4.3.2 Grinding of Taro to Produce Taro Pulp

The use of the motor-driven grinder was considered to be an effective way of grinding the raw material. The grinder was a home design, consisting of a motor driving a steel rod with a spiky surface. A feeding hopper directed the raw material to the surface of the rotating rod. As the rod rotated, it ground the taro into pulp which was directed via a steel tray to a collecting container. The size of the fine ground particles depended on the size of the spikes. This had a direct effect on the final product yields, as the amount of starch extracted depended on the degree of rasping done on the taro tissues. The limitation of this method, however, lies on the fact that it does not allow for the recycling of the pulp after removal of starch. In industrial manufacturing of cassava starch, for example, the pulp is sieved while washing with water, and the pulp is rasped again (Knight, 1969). This second rasping would certainly optimize the yields.

It took 7 minutes to grind all the 98 kg peeled taro *Colocasia* sample into pulp. At this rate, it would take about an hour and a half to grind one ton of taro. So during an 8-hour working day, 6 to 7 tons could be ground. A grinder of this type but having bigger motor and more than one grinding rods, would be suitable in a larger commercial scale taro starch processing.

This grinder was operating on petrol, which was another advantage since electricity is fairly expensive in Tonga. The high energy (electricity) cost has been a drawback to industrial development in the country. Availability of machinery that operates on petrol or any other alternative energy resources would be an economical advantage.

The use of Kenwood blender to grind taro *Colocasia* in New Zealand was less efficient than the use of the home-designed grinder in Tonga. This was mainly due to the smaller size of the blender, and the batch-wise processing of a small amounts

at a time. The blender could only process less than a kilogram of taro at a time. This method would not be suitable for use in Tonga.

4.3.3 The Starch Extraction Process

The starch extraction process used could be considered an effective way of separating starch from the taro pulp. It involved mixing the taro pulp while washing with tap water. The starch was washed off the pulp through fine cheese cloth, which acted as a sieving screen and collected in a tank. This process was done manually, and there was no control on the time of the washing process or on the water flow rate. It was only observed that at the beginning of the washing process, the pulp was very 'thick', and the water did not pass through the pulp easily, so a low water flow was used. After washing for some time, it was observed that the water passed through the pulp very easily, and that relatively clear fluid came through underneath the cheese cloth. The washing procedure would then be stopped, and the remaining pulp discarded.

For *Xanthosoma*, the washing process was relatively easy, and it did not take long (about 20 minutes, depending on the water flow rate which was not measured during the operation) to observe that water passed through the pulp easily and that relatively clear fluid came through underneath the cheese cloth. For *Colocasia* and *Alocasia*, it took much longer time to reach this stage.

In an industrial starch extraction, the extraction could be carried out in a large tank, equipped with a vertical paddle mixer. The pulp may be mixed with excessive amounts of water for a certain period of time to allow complete removal of starch granules from the surface of the small tissue particles of the pulp. The mixture could then be sieved through a screen.

It would be fairly expensive to operate a mixer using a large motor on electricity in Tonga. Installation of mixing facilities which could be operated manually might be a more economical way of carrying out the extraction process.

4.3.4 The Starch Settling Process

After the extraction of starch from the pulp, the starch milk was left for a period of time to allow the starch to settle. For the *Xanthosoma* starch, this process took place smoothly, the starch took around 3 - 5 hours to settle to a solid cake at the bottom of the settling tank, leaving a clear supernatant. However, for the other samples, *Alocasia* and *Colocasia*, the results were virtually the opposite.

In case of the *Alocasia*, it took 10 - 12 hours to observe two separate layers in the starch milk. The top layer was relatively clear, and the bottom layer was white, containing the starch. This bottom layer, however, remained a thick liquid even after 24 hours of settling time. The top layer was removed by means of suction using a hose, and the thickened starch layer was packed in air-sealed buckets and stored in a 5°C cold store. After 24 hours storage, it was found that the starch slurry remained a homogenous thick liquid without further separation occurring. It was therefore decided that this slurry be air freighted to New Zealand for further processing. The starch slurry was separated using a bowl centrifuge (SME 467). It was observed that the decanted liquid was still white, ie. contained a reasonable amount of starch. This contributed to the low yield observed for *Alocasia*.

In the case of *Colocasia*, on the other hand, the result was even more dramatic. The starch milk remained a homogenous solution; there was no settling of starch observed after 72 hours of settling time. This resulted in shipment of raw material (a second *Colocasia* sample) to New Zealand, and the extraction was carried out in the pilot plant (Dept. of Food Technology, Massey University) and the separation of starch from the milk was carried out using the same bowl centrifuge, as used for *Alocasia*.

There was no report of such extreme difficulty in extraction of starch from *Colocasia* and *Alocasia*. Moorthy (1991) reported a relatively longer starch settling time for taro starch, while others (Georing and DeHaas, 1972; Kinjo and Fukuba, 1978; Bradbury and Singh, 1986) did not mention any problems with starch extraction. It seems that the hurdle faced in this study had something to do with the raw material

used which in turn is a function of the soil and climatological conditions and other factors. However this concept was not investigated further.

Starch separation is one of the many applications where sedimentation is used. Sedimentation is a separation of suspended solid particles from a liquid by gravity settling. Two functional operations are distinguished - thickening and clarification. The thickening operation results in an increase in concentration of solid particles in a suspension, while in clarification, the suspended solid is removed leaving a clear effluent. The two functions are similar and occur simultaneously in many operations.

For the best yields and effective application of sedimentation in starch separation, it is desired that clarification be achieved. ie. that all the solids, which are mainly starch granules, be removed from the suspension, and the clear effluent be discarded. In taro starch separation, application of sedimentation resulted in clarification in *Xanthosoma* starch suspension, thickening of *Alocasia* starch suspension, and it did not work for *Colocasia* starch suspension. These results indicated that there is something significantly different between these three taro genera. Other than the presence of mucilaginous material in all of the taro cultivars used, the compositional analysis has shown that these genera had similar compositions, (Bradbury and Holloway, 1988). This problem is yet to be defined.

The particle settling rate is a function of many factors including particle characteristics (size, shape, and density) and medium characteristics (viscosity, composition, pH etc). In order to appoint an appropriate technology for taro starch separation, these factors need to be defined. Hinderance of starch settling was probably due mainly to the mucilaginous materials present. However, further research is required to define precisely the nature of these materials and an appropriate way of dealing with them given the need to extract starch from taro.

It was observed later in the study that the *Xanthosoma* starch granules were relatively large (similar in size to cassava starch granules), while that of *Colocasia* and *Alocasia* were very small (Section 5.2). This could have been another contributing

factor. Franco et al. (1992) showed that larger granules settled faster than the smaller granules using cassava and corn starches. There is no report on the relationship of the granule size/density ratio and settling rate for taro starch. Both the size and density are of course factors which are determined by the internal molecular orientation of the granules.

4.3.5 Starch Separation Using Centrifuge

On arrival in New Zealand, the *Colocasia* sample (raw taro corms) was peeled, washed, and blended using a Kenwood Chef blender. The pulp was then mixed with water, and screened using a cheese cloth, and the starch milk was collected in a container. The starch was then separated from the milk by centrifugation. The use of the centrifuge was more successful than the conventional settling method. The bowl centrifuge effectively removed the starch from the milk of both the *Colocasia* and *Alocasia*. It was observed, however, that there was still some starch expelled with the supernatant.

Bowl centrifuge is only one of the many types of centrifuges available for particle separations. It was not attempted in this study to use any other centrifuge in the starch separation. Details on the technology and use of centrifuges can be found in Morris, 1966; Purchas, 1977; Svarovsky, 1977.

Selection of an appropriate technology for starch separation in Tonga should always consider the cost of electricity as a major constraint. Centrifugation technology is often an expensive technology to employ. The ability to extract starch from taro using a simple gravitational settling would be an advantage.

4.3.6 The Drying Process

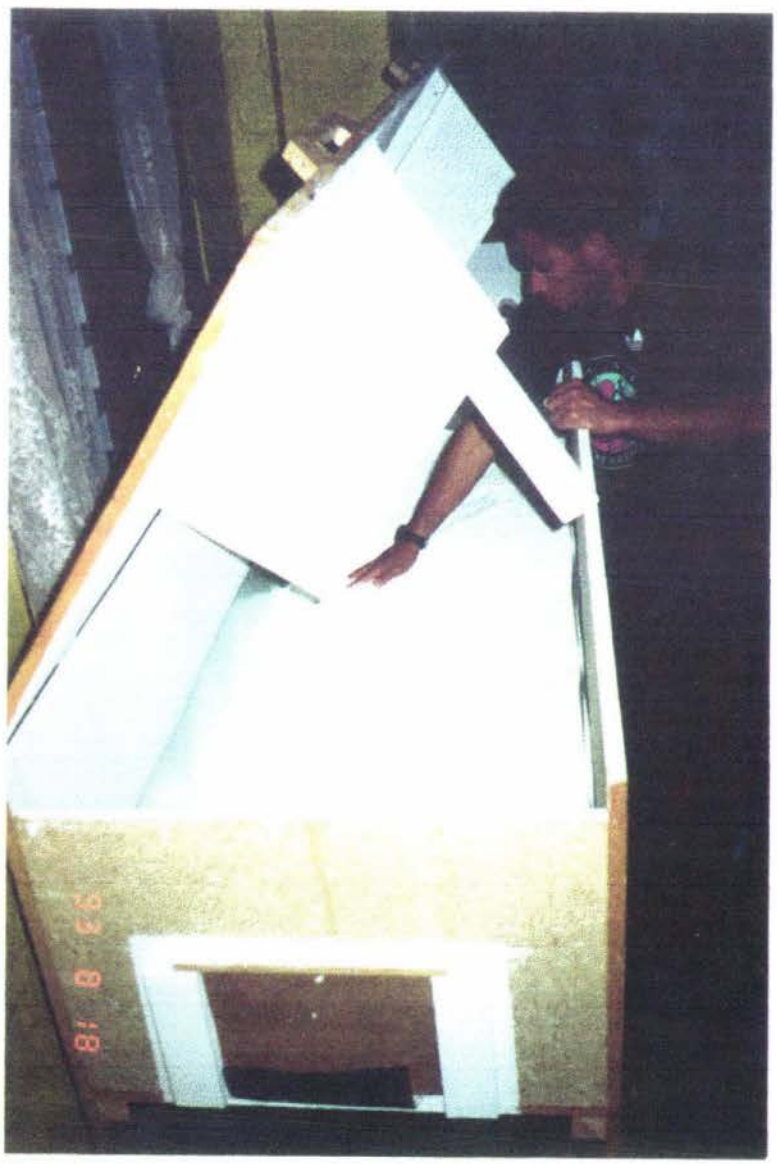
A temporary drier (Figure 4.1) was constructed and used for drying the starch. The weather in Tonga was rainy during the trip, so the construction of the drier was necessary. The drier was constructed from particle board, with a piece of flat iron, covering the bottom of the drier. It was basically a long rectangular box, with baffles coming down from the top to assist the flow of air, and a hot air source at one end and an air outlet at the other end. The top side of the drier was removable to allow for occasional mixing of the starch (Figure 4.3). Two hair driers were used as sources of hot air (Figure 4.2).

Figure 4.1: Hot air drier used to dry starch in Tonga

The inside temperature of the drier as measured by a thermometer, was 38 - 43°C. It was found that after 20 to 24 hours of drying, the starch was dry enough for short term storage, varying between 13.5 - 17.5%.

The use of Whitlock drier in New Zealand for drying the *Alocasia* and *Colocasia* starch was more efficient. The starches were dried using at the same temperature as that used in Tonga (ie. 40°C) but after drying for 18 hours, the moisture contents were between 7 - 9%. This was due mainly to better design and better control of temperature and air-flow, within the drier.

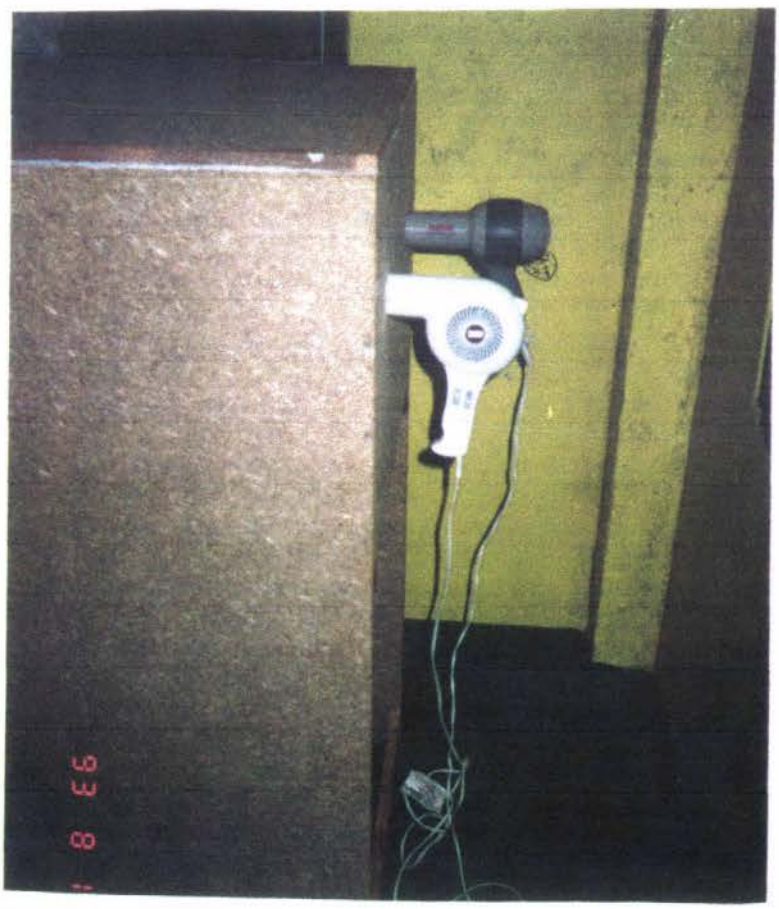
Figure 4.2: Removable top side of starch drier built in Tonga



Ahmed and Lelievre (1978), reported that different drying procedures resulted in different polymer order within the starch granules, which may have some effect on the functional properties of the starches. However, this effect may be insignificant in this study since a comparative analysis was attempted and that the starches were treated the same.

The drying method could be successfully utilized in a commercial processing. The dimensions of the drier were 3.5 m × .85 m × .85 m. It was found that the drier could effectively be used to dry the starch. The inside area of the drier could be smaller. Decreasing the inside area could result in more efficient drying due to higher velocity, and may be higher temperature, which might allow the use of only one drier instead of two. This however, needs confirmation.

Figure 4.3: Hair driers used as sources of hot air in starch drier built in Tonga



4.4 Starch yields

The yields of the starch from the raw materials were 15, 14.5, and 21.6% (wet basis) for *Alocasia, Colocasia*, and *Xanthosoma* respectively. Unfortunately, the starch content was not determined for the raw materials, but assuming that the starch contents for these taro cultivars reported by Bradbury and Holloway (1988) are applicable, then 46, 42, and 66% of the starch were extracted from *Alocasia, Colocasia*, and *Xanthosoma* respectively.

It can be seen that yields were relatively low, particularly for the *Alocasia* and *Colocasia*. There were several factors that contributed to low yields in extraction. It has been mentioned earlier that the starch extraction and separation had affected the yields to a large degree. Another factor was the size of taro particles in the pulp. The grinding process ruptured the starch containing tissues of the taro flesh, releasing starch granules which could be washed off during the extraction process. The yields therefore were a factor of the particle sizes in the pulp. Starch granules that were contained within these particles were not extracted. The larger the particle sizes, the more starch that was not extracted. This factor limited the yield to a large degree, and applied to all the taro samples.

Another factor that contributed to the low yield was the mechanical loss during the processes of starch extraction. This included spillage, incomplete grinding of individual cormels/corms, and other losses of material during transference of materials and other operations.

The starch yields were considered to be relatively high for a laboratory scale operation. Adkins and Greenwood (1966) obtained starch yields of 46 - 66%, dry basis, for a wide range of cereal starches using a similar extraction method. The yields can be improved in an industrial operation by recycling of taro pulp for a second rupturing, and a more efficient way of controlling the other unit operations such as the extraction and separation processes.

It was not a primary objective of this study to design a suitable process for taro starch extraction. However, the information found may be of some help in future studies in Taro starch.

4.5 Starch Purification

A compositional analysis of the raw extracted taro starch was carried out to obtain some information on the level of impurities present in the starch. It was decided the starches be analyzed for protein, fat, and fibre contents. Table 4.2 summarises the results.

Table 4.2: Protein, fat, and dietary fibre contents of raw taro starches (% dry basis)

	Alocasia	*Colocasia*	*Xanthosoma*
Protein	1.12	1.75	0.37
Fat	<0.1	<0.1	<0.1
Total dietary Fibre	0.31	0.12	0.27

There were reasonable amounts of impurities present in the starches. It has been mentioned earlier (Chapter 1) that taro contains 3 - 10% fibre, and 3 - 6% protein on a dry basis, with very little fat. It can be seen that a significant amount of protein was associated with the taro starches. For some of the tests for rheological properties, it is crucial to remove all the impurities from the starches. It was therefore necessary to purify the starches, before they could be used for some of the tests.

It is interesting to observed that the protein content correlated well with the ease of extraction and settling of starch among the three samples. Bradbury and Holloway, (1988), reported the presence of relatively large amounts of proteins in various cultivars of taro. Hammer (1987), reported that these large amounts were due to the

presence of trypsin and chymotrypsin inhibitors. The presence of proteins may be another factor that contributed to the difficulty of extraction of starch, as suggested by Moorthy, 1991. It was not attempted in this study to define this phenomenon in more detail.

There was little fat in the taro starch. Compositional analysis on various cultivars of taro had shown that there were 0.04 to 0.1% of fat in whole taro flesh, depending on the cultivar (Bradbury and Holloway, 1988; Maga, 1992). One would expect the starch to contain even less fat. The amounts of fat in the extracted taro starches, as shown in the table, were negligible. However, the fat extraction procedure in the purification process was carried out anyway, but for a relatively shorter period (6 hours) than the period, 24 hours, recommended by Adkins and Greenwood (1966).

There were considerable amounts of total dietary fibre in all the starch samples. This may probably have been due to the manual operation of the starch extraction where the starch was forced by the actual mixing of the taro pulp through the micro-holes of the cheese cloth used. This could have allowed fragments of fibre to pass through the cloth and be collected with the starch. However, this fibre, could easily be removed by the washing procedures during the purification process. The microholes of the cheese cloth used for starch extraction were not measured. However, judging from the visual appearance, the final product (dried starch) was considered to be highly acceptable in terms of its crystal white colour and physical features.

The first washing steps were to remove all residual impurities that may have been present in the starch. After shaking with toluene, the toluene layer should have contained protein and some fat (Adkins and Greenwood, 1966). The fat extraction procedure (ie. refluxing with aqueous methanol) was provided to remove any fat present in the starch samples.

After the purification process the starch samples were reanalysed for protein, fat, and total dietary fibre and there was <0.1% for fat, protein and fibre in all of the starch samples. These results showed that the purification process had effectively removed the impurities that were likely to affect the functional properties of the starches. These results were considered acceptable.

4.6 Conclusion

The *Xanthosoma* starch was effectively extracted by a simple washing extraction and settling procedure. The *Alocasia* and *Colocasia* starch extraction required the use of centrifugation. The starch extraction procedure yielded a 15, 15, and 22% (wet basis) starch recovery for *Alocasia, Colocasia*, and *Xanthosoma* respectively. The impurities present in the raw starch were effectively removed by the purification method used.

CHAPTER FIVE

PHYSICAL AND MOLECULAR CHARACTERISTICS

5.1 Introduction.

Banks and Greenwood (1975), reported that the properties of starch granules are related to a combination of two factors: the chemical constitution, which depends on the presence of amylose and amylopectin molecules, and the physical constitution, which involves the organization of these polymers to form a unique structural entity (granule physical structure). It is therefore important in studies of starches to define these aspects.

In this part of the study, an attempt was made to define to some degree the physical and molecular characteristics of the starches under investigation. The taro starch samples (*Alocasia, Colocasia*, and *Xanthosoma*) were analyzed together with cassava starch in order to provide some reference.

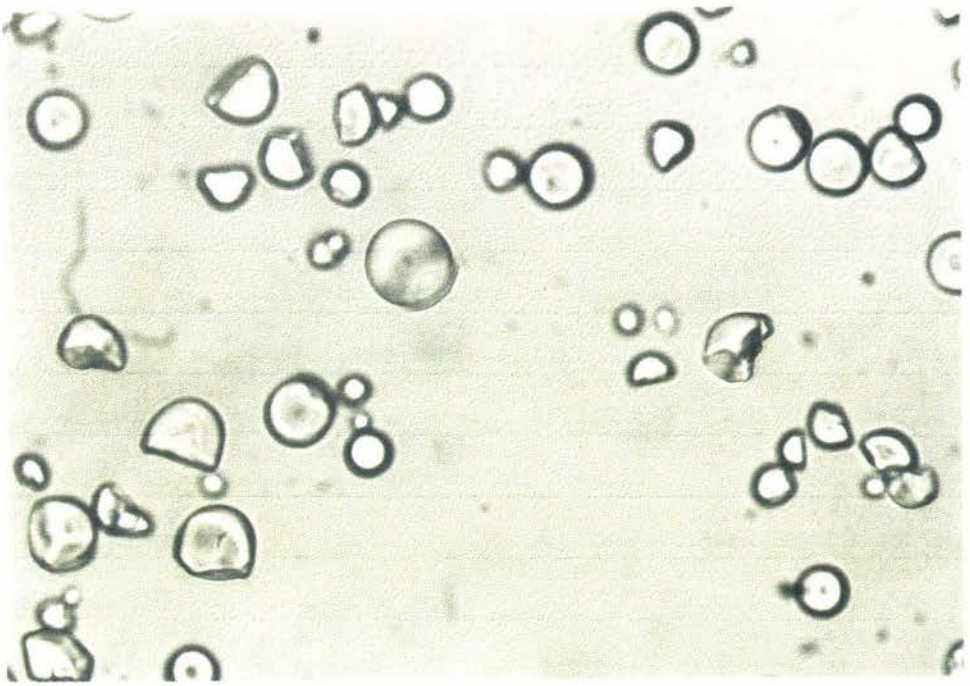
5.2 The Starch Granule Physical Characteristics

The physical structure of starch granules was studied using light microscope.

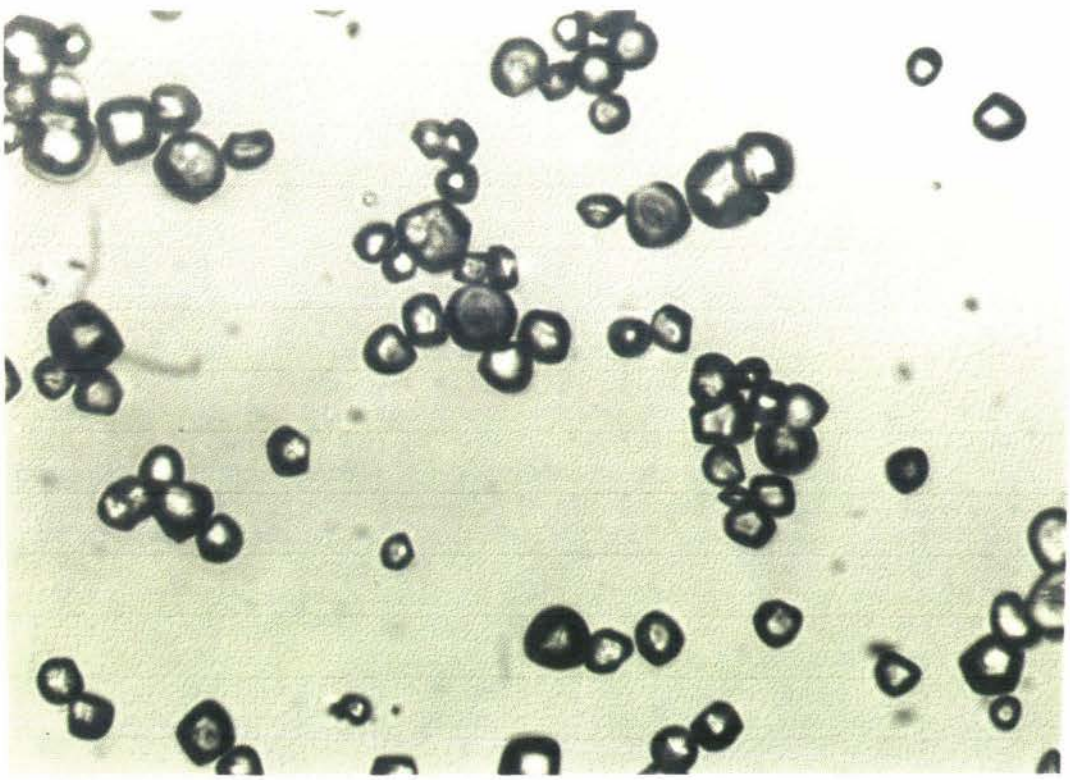
5.2.1 Results

Figure 5.1 presents photomicrographs of the starch granules (under the same magnification).

Figure 5.1: Photomicrographs of Taro starch granules, under (× 10,000) power magnification .

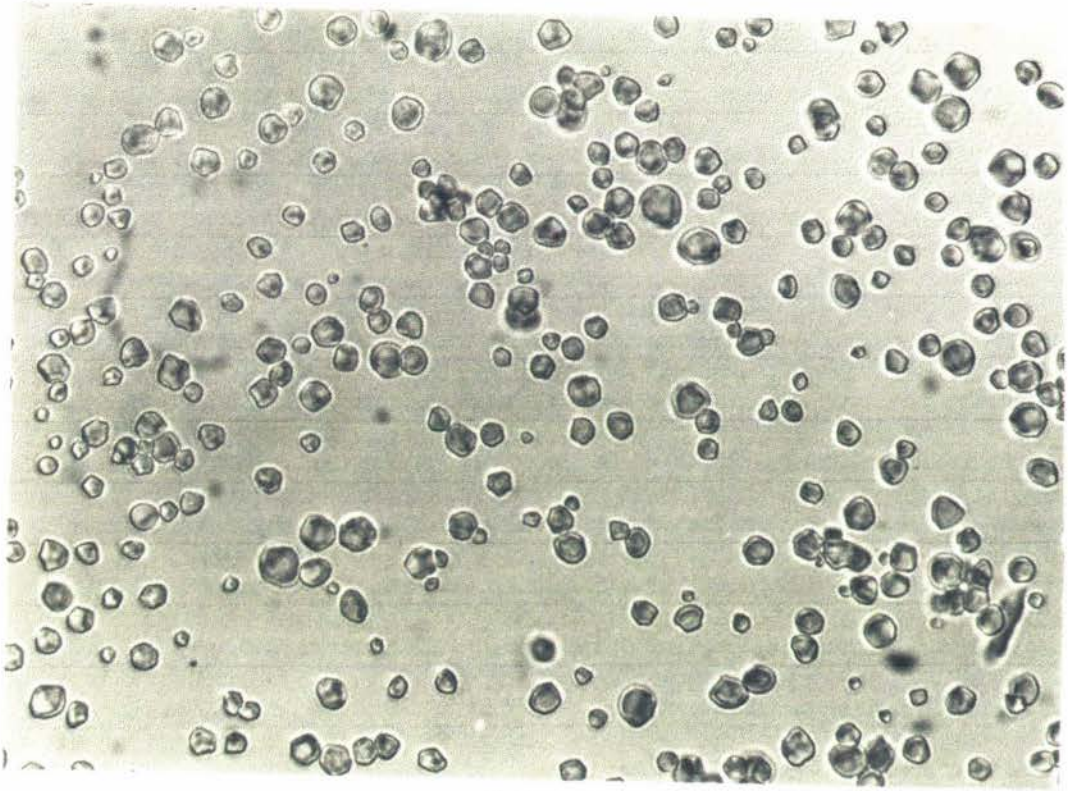


Cassava

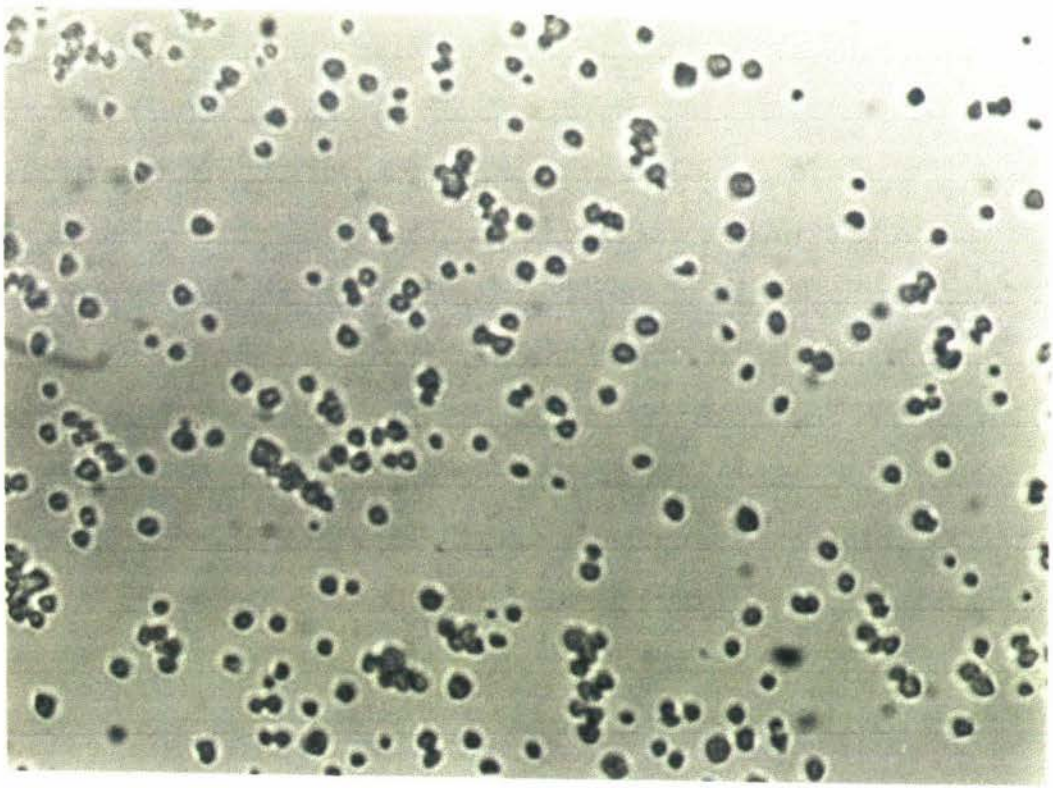


Xanthosoma

Figure 5.1: Continue



Colocasia



Alocasia

Table 5.1 summarises the starch physical and molecular characteristics.

Table 5.1: Physical Characteristics of Starch Granules

	Cassava	***Alocasia***	***Colocasia***	***Xanthosoma***
Granule Shape	round oval	polygonal	polygonal	polygonal round
Granule size (μm)	5-35	0.5-3	0.5-6	5-30

5.2.2 Discussions

It can be seen from these results that the granule shape of all the three taro starches were polygonal as opposed to that of the cassava which was round or oval. Several starches have been reported to be of similar polygonal shape to those exhibited by the taro starches including: rice, sweet potato, and some maize starches (Knight, 1969).

The granule sizes were strikingly different among the three taro starches. The *Xanthosoma* starch granules were relatively large (5-30μm) and similar to that of cassava (5-36μm). The granules of both *Colocasia* and *Alocasia* were relatively small, 0.5-6 and 0.5-3μm respectively. The starch granule shape and size of the *Colocasia* cultivar was similar to that reported by other workers for various other *Colocasia* cultivars (Georing and DeHaas, 1972; Kinjo and Fukuba, 1978; Sugimoto et al., 1986; Sugimoto et al., 1987; Maga, 1992; Moorthy et al., 1993). There were no reports, however, on the starch granule size and shape of cultivars of *Xanthosoma* and *Alocasia*. It was interesting to find that the granules of *Alocasia* starch were even smaller than that of *Colocasia*.

There are many applications of starches in the food industry that is related to their sizes. The small size of starch granules provides suitability for certain applications. It has been mentioned in Chapter 1, that the small size of taro starch granules has been proved to be accountable for its high digestibility which makes taro suitable for baby foods. Griffin and Wang (1983) have discussed the suitability of taro starch,

because of the small granules, for other industrial applications such as in cosmetic industry and in plastic industry. The advantages of using taro starch granules in plastic production include: density comparable with plastics, low porosity, very low abrasive properties, not water soluble, low fixed gas permeability, and biodegradability (Plucknett, 1970). All of these advantages are due to the very small particle size of the taro starch granules.

5.3 Amylose Content

5.3.1 Introduction

One of the most crucial information that is required for successful studies on the functional properties of starches is their molecular structure. In particular, the amylose and amylopectin contents. It has been mentioned earlier that starches are made up of two main type of polysaccharides: amylose and amylopectin. Banks and Greenwood (1975) have also reported the presence of up to 10% of a third component in some starch (eg. amyl-maize starch) which gives special characteristics such as poor stability in aqueous solution. The molecular structure of starches, dictates most of their functional properties. In most starches only amylopectin and amylose molecules are present. It was considered in this study that a determination of either amylose or amylopectin content was necessary. The amylose contents were treated as an indication of the relative proportions of the two polysaccharides in the test starches.

In this study, an attempt was made to determine the amylose content of the test starches using the method of Morrison and Laignelet (1983). This method was a colorimetric determination of amylose based on a blue polyiodide complex. The blue values (absorbances) were converted to % amylose content using the following general equation (The equation was derived from regression of blue values of known amylose-polyiodide concentrations) :

$$\% \text{ Amylose} = (28.414 \times \text{Blue Value}) - 6.218$$

The blue value was the absorbance/cm at 20°C of starch-iodide complex, measure at λ = 635nm. Measurements at higher temperature had to be converted to blue values at 20°C using correcting factors which depended on the differences between the measuring temperature and 20°C. The method was followed in exactly the same way as reported by Morrison and Laignelet, 1983.

5.3.2. Results

Table 5.2 summarises the results of duplicate samples of each starch analyzed for amylose content.

Table 5.2: Amylose contents of Taro Starches

Starch	Sample	Blue Value[1]	% Amylose	Average
Cassava	1	0.9124	19.71	19.79
	2	0.9184	19.88	
Alocasia	1	0.6447	12.10	12.09
	2	0.6438	12.07	
Colocasia	1	0.7026	13.75	13.60
	2	0.6924	13.45	
Xanthosoma	1	1.1732	27.12	27.42
	2	1.1950	27.74	

1 = Blue value (absorbance/cm at 635nm) at measuring temperature converted to blue value at 20 °C (Morrison and Laignelet, 1983).

5.3.3 Discussion

The results showed very close agreements between the of the duplicate samples. It can be seen that the *Colocasia* and *Alocasia* starches contained similar amounts of amylose, 13.6 and 12.1% respectively. The amylose content of *Colocasia* starch was consistent with 13.5 and 10.8% amylose contents reported by Sugimoto et al. (1986) for starches of two different cultivars of *Colocasia*. Moorthy et al. (1993) reported

a range of 14 to 19.4% amylose content when analyzing ten different cultivars of *Colocasia*. However, this percentage (13.5%) was relatively high compared with 7-10% reported by Kinjo and Fukuba (1978). The differences may be attributed to different methods of amylose determination and different cultivars used in different studies. There was no report on the amylose content of *Alocasia*.

The *Xanthosoma* starch exhibited a strikingly higher amylose content than all the other test starches. It contained even higher amylose (27.4%) than cassava starch (19.8%). It is interesting to note that other than cassava starch, the amylose content of the taro starches followed the same order as that for granule size. The *Xanthosoma* starch had much larger granule size and amylose content than both of *Alocasia* and *Colocasia* starches, similar to cassava starch. The *Colocasia* and *Alocasia* starches had similar granule sizes and amylose contents. The amylose content of cassava starch was found to be similar to the reported range of 16 - 18% (Balagopalan et al. 1988). Although there seemed to be a relationship between amylose content and the granule size in this study, Moorthy et al. (1993) had demonstrated that there was no relationship between amylose content and granule size. It was not attempted to investigate this concept further.

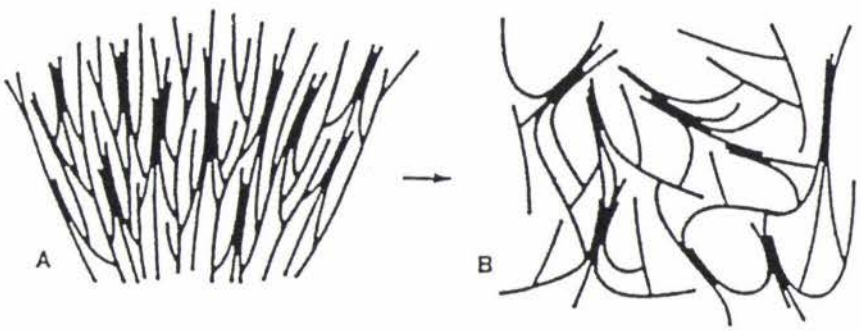
5.4 General Discussions

The functional properties of starches are closely linked to the amylose:amylopectin ratio within the starch granules. The amylose and amylopectin molecules are oriented in the starch granule in a radial fashion (Sterling, 1978). The amylose molecules or the linear portions of the amylopectin may be laid closely to each other forming hydrogen-bonds between adjacent segments (Wurzburg, 1986). These areas of parallel fashioned association create radially oriented micelles. A long linear chain may pass through several micelles, or the outer fringes of a single branched molecules may participate in a number of micelles, Figure 5.2, (Pomeranz, 1985). These micellar crystallites are responsible for the granular integrity and for imparting birefringence properties which are manifested by polarization crosses (Wurzburg, 1986). During gelatinisation the granules swell as molecules disorient themselves.

Between the more organised crystalline regions are more loosely packed amorphous regions (Pomeranz, 1985).

Both of these regions play vital roles in determining the functional properties of a given starch. In gelatinization of starches, the intermolecular forces that bind the starch molecules in both the amorphous and crystalline regions determine the gelatinization properties of the starches. In starch gels, the interaction of swollen granules, which are made up mainly of amylopectin, and the amylose matrix, in which the swollen granules are embedded, determine the properties of the gels.

Figure 5.2: Micellar structure and mechanism of swelling of starch granule



Micellar structure and mechanism of swelling of the starch granule. (A) Segment of an unswollen granule, with associated micelles represented as thickened sections. (B) Segment of a swollen granule, showing disoriented but still persistent micelles.

Given the amylose contents of the taro starches, one would expect the *Xanthosoma* starch, because of high amylose content, to gelatinize at a higher temperature than that for cassava starch, to form a very strong gel and highly susceptible to retrogradation. The *Alocasia* and *Colocasia* were both expected to exhibit similar gelatinization and gelling properties, and to have weaker gel, but less susceptible to retrogradation than *Xanthosoma*. The subsequent chapters discuss different experiments undertook to investigate the functional properties of the starches and to explore these expectations.

5.5 Conclusions

All the taro (*Xanthosoma, Colocasia*, and *Alocasia*) starches exhibited similar granule shape. The granule shape was polygonal. The *Xanthosoma* starch exhibited a similar granule size (5-30μm) to that of cassava starch granules (5-35μm). The *Colocasia* and *Alocasia* starches exhibited similar granule sizes, 0.5-6μm and 0.5-3μm respectively. The amylose contents of the test starches were: *Xanthosoma* 27.4%, *Colocasia* 13.6%, *Alocasia* 12.1%, and cassava 19.8%.

CHAPTER SIX
STARCH GELATINIZATION

6.1 Introduction

Most of the industrial applications of the starches are determined by their gelatinization properties. The starches under investigation, were studied, together with cassava starch as reference, for their gelatinization properties. Various techniques were employed to investigate the gelatinization of the test starches and this chapter discusses the findings.

6.2 Sensory Evaluation

6.2.1 Introduction

This method of evaluation of the starch gelatinization has been described in Section 3.4.1. This attempt was carried out mainly to provide some preliminary results and to give some ideas as to what temperature the starch commenced gelatinization. The gelatinization temperature was taken as the temperature at which the cloudy paste started to become clear. The gelatinization temperature could not be determined because the end of the gelatinization range, ie. when all the starch granules were effectively gelatinized, could not be visualised, hence noting the end temperatures. The temperature measurement was done manually using a mercury glass thermometer, and the gelatinization temperatures were recorded based on visual observation.

6.2.2 Results

Table 6.1 shows the gelatinization temperatures for the test starches. The gelatinization temperature was taken as the temperature at which the starch slurry was first recognised to start losing its opacity, and started getting thicker. The mean of three measurements were taken as the gelatinization temperature of each starch.

Table 6.1: Gelatinization Temperature (manually measured)

Sample	Gelatinization Temp. (°C)	S.D.
Cassava	69.3	0.9
Alocasia	70.9	1.0
Xanthosoma	75.5	1.2
Colocasia	80.4	1.5

6.2.3 Discussion

The heating process was, measured using a mercury thermometer, about 1 - 2°C/min. Because of this low heating rate, the onset of gelatinization took place over a reasonable period of time (1 - 2 minutes) the onset of gelatinization could be recognised and noted the temperature. The change in viscosity during the early stage of gelatinization, could not be detected. But measuring gelatinization temperature based on commencement of losing opacity can be said to be accurate to within ± 2°C.

It can be seen that the gelatinization temperatures of all the taro starches were higher than that of cassava. The gelatinization temperatures of cassava and *Alocasia* starches were similar, 69 and 71°C respectively. The gelatinization temperature of *Colocasia* was 10°C higher than that of *Alocasia* and 5°C higher than that of *Xanthosoma* starch. This was surprising as from the molecular structure, the *Xanthosoma* starch was predicted to have the highest gelatinization temperature because of highest amylose content. The Alocasia and Colocasia starches were also predicted to have similar gelatinization temperatures. The cassava starch showed the lowest gelatinization temperature, but had the second highest amylose content. This results showed that the temperatures at which the onset of gelatinization occurred in the starches were not necessarily a factor of the molecular structure.

The above given results served only as a guide. The gelatinization temperatures of the test starches were expected to be some where close to the measured values shown in Table 6.1. These results, however, needed further confirmation using more

commonly used reliable methods. Therefore the following further investigations were carried out.

6.3 Hot Stage Microscope

6.3.1 Introduction

In the hot stage microscope method, the measurement of the gelatinization temperatures were base on visualising individual starch granule undergoing gelatinization. The gelatinization temperature was taken as the temperature at which the individual granules started to 'burst' losing their granular integrity. The method for sample preparation and measurement has been given in Section 3.4.2.

6.3.2 Results

Table 6.2 presents the gelatinization temperature ranges for the starch samples as measured using the hot stage microscope.

Table 6.2: Gelatinization Temperature (Hot-Stage Microscope)

Samples	G. Temp. (°C)	S.D.
Cassava	67.2	1.4
Alocasia	69.3	0.9
Xanthosoma	76.3	1.1
Colocasia	80.4	1.3

6.3.3 Discussion

The results presented in this table were very similar to those obtained by the sensory evaluation. It was a little easier to measure the gelatinization temperature using this method. It was easy to see an individual granule "disappearing" as it lost its granular integrity, and hence noted the temperature. It was not easy, however, to note the temperature at the end of the gelatinization temperature range for all the starches. This was mainly because the "disappearing" of a large number of granules happened

fairly fast at the end of the range. The granules seemed to be slowly "disappearing" or "bursting" at the onset of the gelatinization and up to a point when they quickly formed the uniform background mass of the field under the lens, within a few seconds.

The results showed that the starches were different in terms of their gelatinization temperatures. Confirming the results in the previous section, cassava and *Alocasia* starches had similar gelatinization temperatures. The gelatinization temperature for *Colocasia* starch was the same as that obtained in the previous section. The gelatinization temperatures for all cassava, *Alocasia* and *Xanthosoma* starches were very similar to those reported in the previous section and lower by few degrees than those observed using the previous method. This could be expected since in this method, the very beginning of the gelatinization could be visualized and noted as individual granules "disappearing" as they swelled losing their granular integrity. In the previous method, it would probably take thousands of gelatinized granules to physically show a loss of opacity in the starch slurry during heating. The onset of gelatinization could be few degrees earlier than noted temperature.

6.4 Brabender Amylograph

6.4.1 Introduction

In this method, the gelatinization of the starches were studied based on the changes in the viscosity during gelatinization. The viscosity was measured in arbitrary units of Brabender Units (BU), and recorded during measurement. The stages and conditions of the measurements has been described in Section 3.4.3. Table 6.3 summarises the amylograph characteristics of the starches.

6.4.2 Results

Figure 6.1 shows the Brabender Amylograms of 10% starch suspensions of each starch.

Figure 6.1: Brabender Amylograph

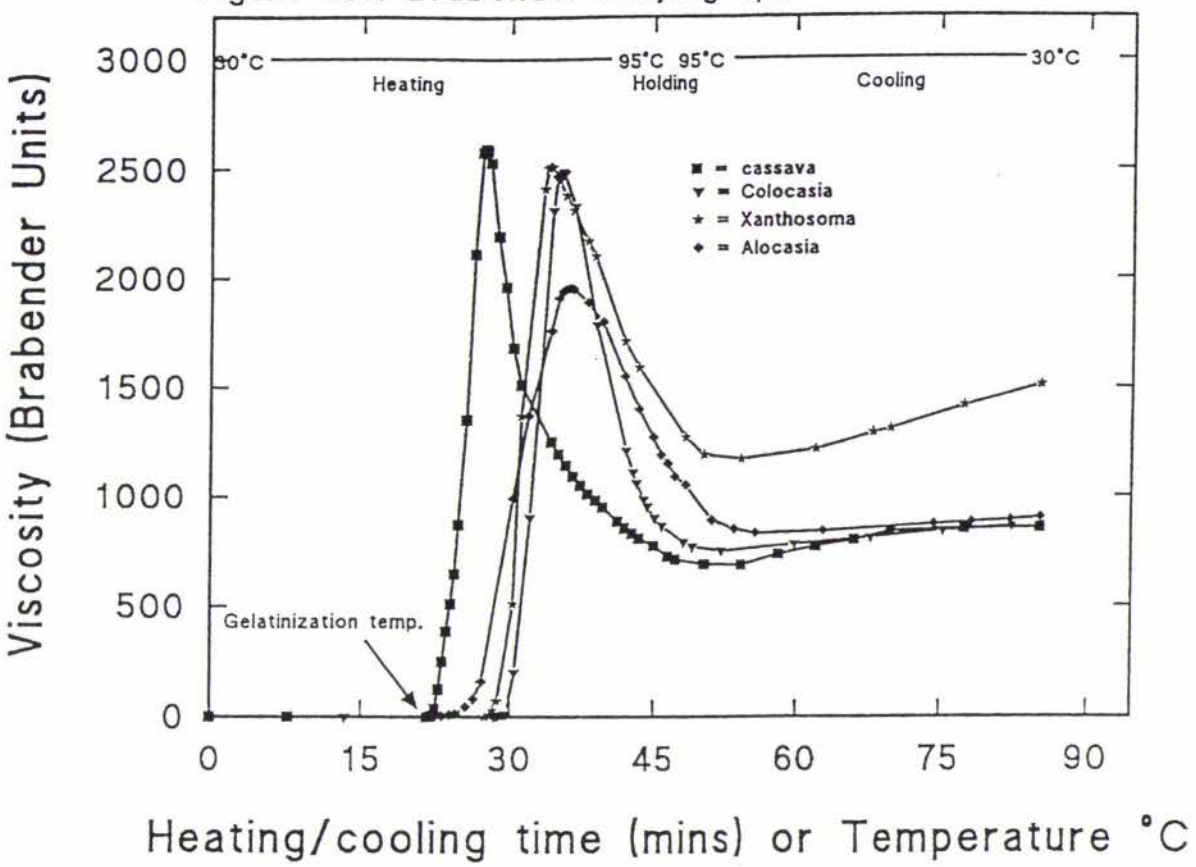


Table 6.3 Brabender Amylograph Characteristics

Characteristics	Cassava	Alocasia	*Xanthosoma*	*Colocasia*
Pasting Temp.[a] (°C)	62.8-71.0	63.0-79.4	71.8-80.9	73.3-82.8
PV (BU)	2595	1955	2515	2490
V_{95} (BU)	808	1165	1590	1060
V_h (BU)	725	1100	1270	770
V_c (BU)	885	895	1520	860

a = Temperature range where pasting of starch gels took place, measured from the temperature at which the viscosity started to increase to the temperature at peak viscosity.
PV = peak viscosity
V_{95} = viscosity at 95°C
V_h = viscosity after holding at 95°C for 5 minutes.
V_c = viscosity after cooling to 30°C.

Note: The actual values of temperatures and viscosity BU were extracted from raw data (not shown) printed out by the amylograph during measurement.

6.4.3 Discussion

It can be seen that the gelatinization temperature (temperature at which the viscosity of the starch slurries started to increase) for all the test starches were lower than those recorded using the former methods. Since the former methods relied only on visual observation, it is likely that the gelatinization could have started at a lower temperature without affecting the appearance of the pastes or showing recognisable changes in the starch granules. In the sensory evaluation method (Section 6.2), noting the gelatinization temperature relied largely on what could be seen. The gelatinization process should have taken place to a certain degree before it could have been visually noticeable. In the hot stage microscope method, the field observed for a given starch showed thousands of granules. Among those thousands of granules, a reasonable number of granules had to be gelatinizing, "bursting", before it could be noticeable. So it is possible that the gelatinization temperature was recorded at a higher temperature than it actually was.

In the Amylograph, on the other hand, the low heating rate (1.5 °C/min) and higher starch concentration (10%) could show any changes in the viscosity accompanying the early stage of gelatinization. However, the results were very similar to those obtained using the previous methods; cassava and *Alocasia* having similar gelatinization temperatures, *Xanthosoma* about 10°C higher and *Colocasia* about 2°C higher still. *Alocasia* starch showed a large pasting temperature range (16°C) compared to the other starches which showed similar ranges of 6 - 10°C.

The pasting temperature for cassava starch (62.8-71.0°C) agrees well with some recorded values: 52-64°C (Knight, 1969), 58-70°C (Balagopalan et al., 1988). However, Moorthy has reported some relatively higher pasting temperature values for cassava: 65-77°C (Moorthy, 1985), 70-90°C (Moorthy, 1991). These figures were both obtained from Brabender Amylograms. The differences may be attributed to varietal variability of cassava. However, this has not been suggested by any worker studying cassava, and it was not clear from Moorthy's latter work why the values were different.

It can also be seen that the cassava starch showed a peak viscosity (2595 BU) higher than all the taro samples. This peak viscosity was reached within about 8 degrees of the gelatinization range. However, as the heating continued it showed the greatest loss of viscosity, to 725 BU after five minutes at 95°C.

Both *Colocasia* and *Xanthosoma* starches showed similar patterns of gelatinization. The viscosity rose to a similar peak value to that of cassava starch paste at a similar rate (slope). However, both of these taro starches started gelatinization at higher temperatures, 72°C for *Xanthosoma* and 73°C for *Colocasia*. Moorthy (1991) reported a relatively high gelatinization temperature for *Xanthosoma*, 81-87°C. The gelatinization temperature for *Colocasia* starch, was similar to that reported by other workers: 73.0°C (Sugimoto et al., 1986), 67-73°C (Moy et al., 1977). Kinjo and Fukuba (1978) reported a value of 78°C, and Moorthy (1991) reported a pasting temperature of 79-88°C. The latter two reports showed relatively higher values. Discrepancies could probably be attributed to either varietal variability or experimental differences.

The *Colocasia* starch showed a loss of viscosity as heating continued, similar to that of cassava starch but at a somewhat slower rate (slope). The *Alocasia* starch did not show the same loss of viscosity on continued heating 95°C, only falling from 1955 to 1100 BU. Cassava, *Alocasia* and *Colocasia* starch pastes showed similar viscosities on cooling, 860 -890 BU.

The *Xanthosoma* starch, on the other hand, lost viscosity to a less degree and at a lower rate than both cassava and *Colocasia*, falling from 2515 to 1270 BU on continued heating at 95°C. Upon cooling, the *Xanthosoma* starch restored viscosity to a larger degree, ie. on cooling the starch gel a relatively larger increase in viscosity was observed, and the final viscosity was nearly twice the viscosities of the cassava *Alocasia*, and *Colocasia* pastes.

The *Alocasia* starch started gelatinization at a similar temperature (63.0°C) to that of cassava starch (62.8°C). This was consistent with the results of the previous methods. It can be seen (Figure 6.1) that the *Alocasia* starch gelatinized slowly as indicated by the slow increase in viscosity (slope). The viscosity of the *Alocasia* starch paste rose relatively slowly to a peak viscosity lower than all the peak viscosities of the other test starches (500 BU lower than *Colocasia* starch), at a temperature higher than the peak viscosity temperatures of the other starches. As heating continued, the viscosity decreased slowly to a value higher than both cassava and *Colocasia* starches, but lower than that of *Xanthosoma* starch. On cooling, the viscosity of *Alocasia* maintained a constant level of similar degree to that of cassava and *Colocasia* gels.

All the starches showed a single stage gelatinization. This suggests a similar molecular orientation within the granules of the starches.

6.5 Differential Scanning Calorimetry (DSC)

6.5.1 Introduction

In this study, the "melting" or gelatinization of starches was investigated using a Perkin-Elmer DSC-7. Details and conditions of the measurement procedure has been described in Section 3.4.4.

6.5.2 Results

Figure 6.3 shows the typical endothermic peaks produced by the DSC for the starch gelatinization. Table 6.4 summarises the results.

Figure 6.2: DSC endothermic peaks of gelatinization

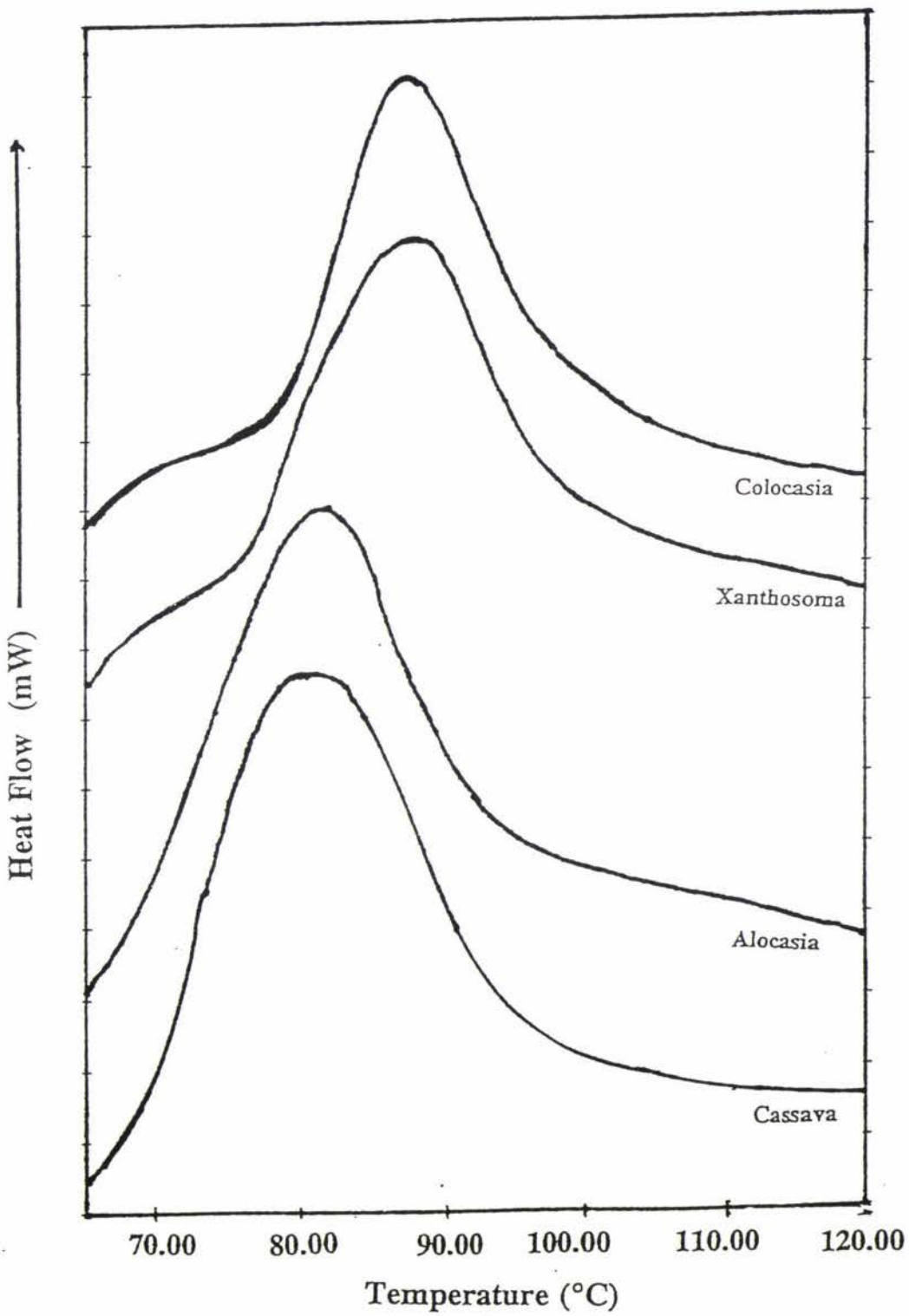


Table 6.4: Gelatinization characteristics of taro and cassava starches measured by DSC.

Cassava Starch Concentration	**No. Samples**	T_o	T_p	ΔH
7%	20	68.8 (0.62)[1]	75.3 (0.86)	0.88 (0.04)
10%	7	69.0 (0.42)	74.6 (0.51)	1.35 (0.11)
20%	10	68.1 (0.55)	74.2 (0.56)	2.73 (0.08)
30%	11	68.2 (0.27)	75.4 (1.05)	3.44 (0.15)
***Alocasia* Starch Concentration**	**No. Samples**	T_o	T_p	ΔH
7%	20	68.9 (0.93)	80.7 (0.62)	0.63 (0.04)
10%	10	69.3 (0.61)	80.0 (0.10)	1.09 (0.02)
20%	8	69.7 (1.08)	80.9 (0.81)	2.53 (0.06)
30%	13	70.1 (0.02)	80.5 (0.06)	3.11 (0.06)
***Colocasia* Starch Concentration**	**No. Samples**	T_o	T_p	ΔH
7%	20	79.1 (0.42)	85.5 (0.32)	0.78 (0.05)
10%	13	78.4 (0.26)	84.8 (0.19)	1.20 (0.08)
20%	8	78.4 (0.31)	85.3 (0.28)	2.08 (0.08)
30%	11	78.7 (0.24)	85.0 (0.26)	3.28 (0.10)
***Xanthosoma* Starch Concentration**	**No. Samples**	T_o	T_p	ΔH
7%	20	74.8 (0.20)	85.6 (0.41)	0.92 (0.01)
10%	10	75.0 (0.22)	85.8 (0.36)	2.03 (0.03)
20%	8	74.9 (0.27)	85.1 (0.31)	3.12 (0.02)
30%	13	75.2 (0.24)	85.5 (0.37)	4.64 (0.02)

T_o and T_p = onset and peak temperatures °C.
ΔH = enthalpy (heat of gelatinization) J/g.
1 = standard deviation

6.5.3 Discussion

T_o and T_p were not affected by increasing the concentration of starch up to 30% w/w in all the starches. It can also be seen from Figure 6.3 that all the test starches showed a single endotherm gelatinization. A discussion of the effect of moisture on starch gelatinization has been dealt with in Chapter 2, (Section 2.7.1). Analyzing gelatinization of rice starch using DSC, Wirakatakusumah (1981) observed a shift of T_o to a higher temperature and a broadening of the gelatinization temperature range (T_p-T_o), with higher starch concentration, $\geq$ 33%. This does not appear to be the case with Cassava and Taro starches at least up to 30% concentration.

All the gelatinization temperatures for the test starches were observed to be higher than those observed using the Amylograph but similar to those measured using sensory measurement and the hot stage microscope. The difference in gelatinization temperature as measured by Amylograph and DSC was also reported by Lund (1984). Other workers have also reported different gelatinization temperatures when using different techniques, (Kinjo and Fukuba, 1978; Sugimoto et al., 1986).

The differences in the gelatinization temperatures as measured by the DSC and the Amylograph may be attributed to the heating rates used. In the DSC the heating rate was 20 °C/min whereas in the Amylograph the heating rate was 1.5 °C/min. The high heating rate in DSC may have caused overshooting which resulted in a higher gelatinization temperature observed (Lund, 1984).

Although there were differences in the gelatinization temperatures reported from the DSC measurement, it can be seen the test starches still retained the same order of gelatinization temperature as that observed using the Brabender Amylograph, and the other methods namely, cassava < *Alocasia* < *Xanthosoma* < *Colocasia*. This provides information about the relative associative molecular forces that constitute the granules of each starches.

From this order there was obviously no correlation between gelatinization temperature and granule size as the *Xanthosoma* and cassava starches had similar granule sizes (5-35 μm) but Alocasia and Colocasia granule sizes were much smaller (0.5-6 μm). The amylose contents of the starches did not appear to correlate well with the gelatinization temperatures. The *Xanthosoma* and cassava starches could be expected to have strongest intermolecular binding forces because of high content of linear molecules (amylose), 27.4 and 19.2 respectively. It can be seen that this was not the case. Furthermore, *Colocasia* starch having a relatively low amylose content, exhibited the highest gelatinization temperature.

However, there was a very strong relationship between the amylose contents and the enthalpy of gelatinization (ΔH). The enthalpy of gelatinization was considered to be a more realistic indication of the intermolecular binding forces within the starch granules. The enthalpy (ΔH) was a direct measure of the actual energy required for a complete gelatinization of the whole granule population within the starch sample. The gelatinization temperature was only a measure of the onset of gelatinization which could be affected by a wide range of factors. For example, a starch sample with large proportion of mechanically damaged granules would show a relatively low gelatinization temperature regardless of the molecular structure.

It can be seen from these tables that the *Alocasia* and *Colocasia* starches had similar heat of gelatinization (0.63 and 0.78 J/g respectively) and lower amylose contents (12.1, 13.6% respectively). *Xanthosoma* and cassava starches, on the other hand, showed relatively larger heats of gelatinization (0.92, 0.88 J/g respectively), corresponding to higher amylose contents. This suggested that there could be similar type of intermolecular forces within the granules of *Colocasia* and *Alocasia* starches, and that there were similarly stronger intermolecular binding forces existing within the granules of *Xanthosoma* and cassava starches.

The gelatinization temperature range as indicated by (T_p-T_o) can be seen to be fairly similar to that obtained by the Brabender Amylograph. The pasting temperature for *Alocasia*, again cover a relatively wider range. The pasting temperature range of

Colocasia and cassava starches are similar. The gelatinization temperature range of *Xanthosoma* starch was somewhere midway between that of cassava starch and *Colocasia* starch. These observations were in close agreement with those made earlier using the Amylograph.

6.6 Swelling Power

6.6.1 Introduction

Swelling of starch granules is a process associated with the gelatinization of a starch-water suspension. When a starch-water suspension is heated, the water is absorbed by the granules causing the swelling of the granules (Biliaderis, 1992; Waniska and Gomez, 1992). It has been mentioned earlier that this swelling process occurs dramatically at the gelatinization temperature (Miller et al., 1973). The degree to which the granules of a given starch swell is dictated by the molecular orientation and the intermolecular binding forces within the starch granules. Because of these, it follows that the swelling properties of the starch is a characteristic of botanic origin. Therefore a measurement of the swelling property would present information about the internal nature of the granules of a given starch.

The swelling power, as mentioned earlier (Section 3.4.5), is defined as the maximum increase in weight which the starch undergoes when allowed to swell freely in water at a specified temperature. It is expressed as weight of water absorbed per weight of dried starch, g H_2O/g dried starch, (Kulicke et al., 1989). In this study, the swelling power of the starches was measured at 85°C following the standard method by Schoch (1964).

6.6.2: Results

Duplicate samples of each starch were analyzed. The swelling power was taken as the average of the two calculated results. Table 6.5 summarises the results

Table 6.5: Swelling power of cassava and taro starches at 85 °C

Starch	Swelling Power g H_2O/ g starch	Average
Cassava	23.50 23.02	23.26
Alocasia	17.44 16.60	17.20
Colocasia	16.91 15.95	16.25
Xanthosoma	15.16 15.61	15.39

6.6.3 Discussion

It can be seen that cassava starch showed the highest swelling power. This is consistent with the results obtained from the Amylograph where it exhibited the highest peak viscosity, and gelatinized at a low temperature. The water molecules penetrated with less difficulty allowing the granules to swell to a higher extent.

It was interesting to note that although cassava starch had a relatively high amylose content (19.8%), compared to *Colocasia* (13.6%) and *Alocasia* (12.09%), it exhibited a relatively high swelling power at 85°C. It is generally considered (Balagopalan et al., 1988) that for a starch containing high amylopectin (low amylose), the granules are expected to have a high proportion of amorphous regions because of the branched structure of amylopectin molecules. Water molecules would penetrate the granules with less difficulty, hence allowing greater swelling. Furthermore, the amylose would be solubilised in the water phase leaving the amylopectin to form the loosely packed structure of the swollen granules.

It is suggested that the high swelling power of cassava starch compared with *Colocasia* and *Alocasia* starches (which exhibited less amylose contents) may probably be attributed to granule size rather than molecular structure. It has been shown in Table 5.2 that the granule size of cassava starch was 6 to 10 times larger than that of both *Colocasia* and *Alocasia* starches. Because of this large granule size, it would be expected to take up more water on swelling.

However, the taro starches appeared to exist a relationship between swelling power and amylose content. The *Xanthosoma* starch with highest amylose content exhibited the least swelling power. Although the granule size was similar to that of cassava starch, its very high amylose content restricted its swelling power to a relatively low value. The Colocasia and Alocasia (with similar amylose contents) exhibited similar swelling power.

6.7 General Conclusions

The comparative order of gelatinization temperatures was: cassava (69 ± 2°C), *Alocasia* (70 ± 2°C), *Xanthosoma* (75 ± 2°C) , and *Colocasia* (80 ± 2°C). The gelatinization temperature varied according to method used, Brabender Amylograph showed the lowest and DSC showed the highest gelatinization temperatures. The pasting temperature ranges were varied among the test starches. From the Brabender Amylograph results, the pasting temperature range for *Alocasia* was very wide (16°C) as compared with 8, 9, and 10°C for cassava, *Xanthosoma*, and *Colocasia* starches. The gelatinization temperature ranges were 63 - 71, 63 - 80, 72 - 81, and 73 - 83°C, for Cassava, *Alocasia, Xanthosoma*, and *Colocasia* respectively. The swelling power (g H_2O/ g dried starch, measured at 85°C) were *Xanthosoma* 15.39, *Colocasia* 16.25, *Alocasia* 17.20, and cassava 23.26. The enthalpy of gelatinization (ΔH, J/g) increased with increasing starch concentration, and were varied among the test starches. The comparative order enthalpy (which was the same for all starch concentrations) were *Xanthosoma*, Cassava, *Colocasia*, and *Alocasia*. The enthalpy was directly related to the amylose contents of the starches.

CHAPTER SEVEN
THE FUNCTIONAL PROPERTIES OF THE TARO STARCH GELS

7.1 Introduction

Starches, after gelatinizing, may undergo further processing or storage allowing further changes in the nature of the starch gel. In this study attempts were made to describe the test starches in terms of their gelling properties, and the variations in the gel properties during storage at different temperatures. This chapter discusses the findings.

7.2 Gel Strength

There were two methods employed in measuring the gel strength: rheological measurement using a Bohlin VOR Rheometer, and tensile and penetration strength measurement using an Instron Universal Testing Machine.

7.2.1 Rheological Measurement

Rheological properties of food systems is a very important attribute. The texture of foods such as gravies, sauces, soup, and mayonnaise, for examples, is defined solely in terms of their rheological properties. Most applications of various biopolymers including starch and many other polysaccharides and proteins are due to their ability to provide textural rheology to the food systems, rather than their nutritional values. Because of this important consideration, it was therefore desired to describe the test starches in terms of their rheological properties.

In this study, a scan of the sample over a temperature gradient of 25 to 90°C at a rate of 3 °C/min was used. This measurement provided information not only about the relative values of the above variables for the test gels, but also how they varied when heating over the given temperature range. This information is useful as many starch gels are used in products where they are heated before consumption. In these

cases, information about the rheological properties of the gels after heating becomes useful.

The measurements were made every 30 seconds as described in Section 3.5.2. Since all the rheological parameters defined in Section 3.5.2 are interrelated, in most rheological measurement, only the G* and the phase angle are considered. All rheological measurements were carried out under the same conditions.

7.2.2 Instron measurement

In this experiment the gel strength was measured by directly measuring the maximum force required for the cone shaped device (Figure 3.15, Chapter 3) to penetrate through the gel. The force required to penetrate the gel is of course affected by factors other than the strength and rigidity of the gel. These include the shape and size of the sample, the size and shape of the penetrating device. It is therefore important to define these factors when referring to results from these kind of measurements. In this study, the primary objective was basically to compare relative strength of the gels. It was therefore important to be consistent in the method used and the size of samples. This was achieved by using the same sample size, measuring device, and conditions for all the measurements (Section 3.5.2).

7.2.3 Results

Figure 7.1 shows the gel strength of the gels as measured by the G* modulus (Pa), when 5% starch gels were studied over the temperature gradient of 25 - 90°C.

Figure 7.1: Complex Modulus G* of 5% Starch Gels, A Measure of Gel Strength

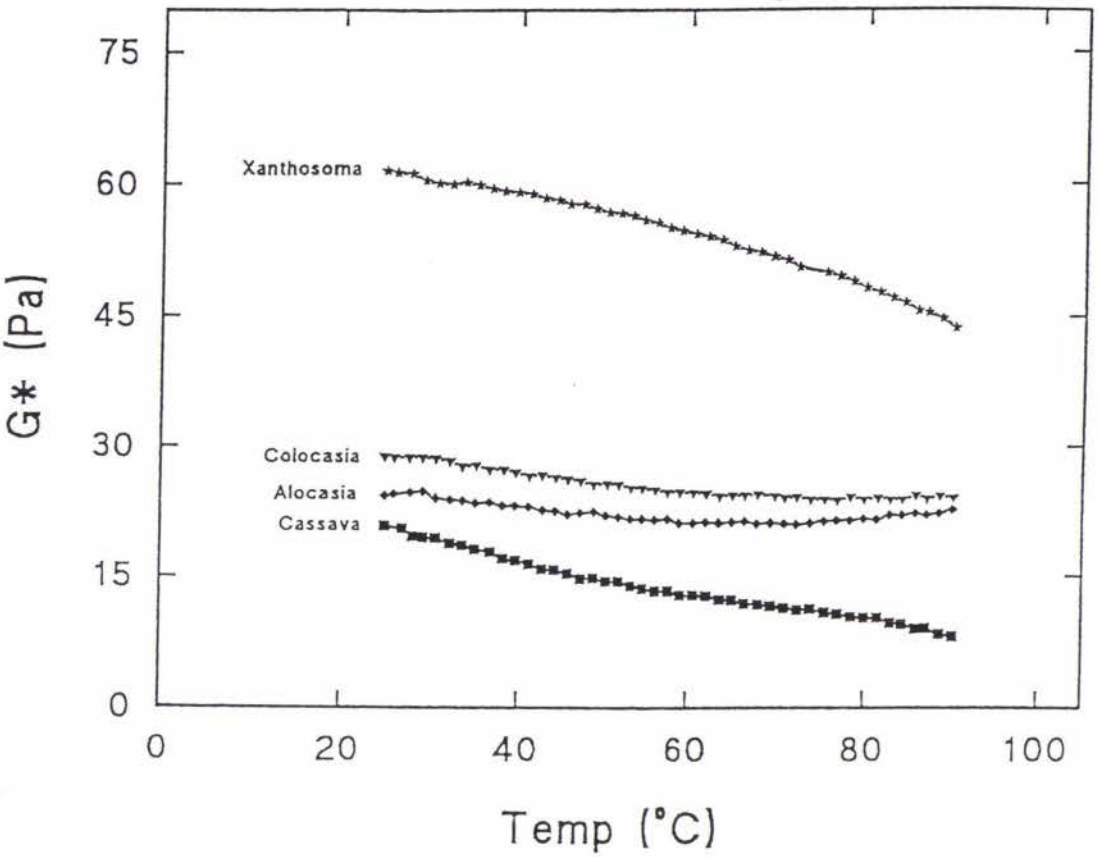


Table 7.1 summarises the results.

Table 7.1: Complex modulus G* (Pa) of 5% w/w starch gels at 25 and 90°C.

Starch sample	Complex modulus G* (Pa) at 25°C	at 90°C	ΔG* ($G^*_{25°C}$ - $G^*_{90°C}$)
Cassava	*20.8*	*8.1*	*12.7*
Colocasia	28.8	24.0	4.8
Alocasia	33.3	30.1	3.2
Xanthosoma	61.5	43.0	18.5

The order of magnitudes of G* at 25°C varied from about 21 to 62 Pa. The *Xanthosoma* gel showed a significantly higher modulus G*, than the other gels.

Table 7.2 shows the recorded maximum forces that were required to penetrate the freshly prepared starch gels.

Table 7.2: Measured penetrating force (N) required to plunge the starch gels

	Force (N)	**S.D.**	**No. samples.**
Cassava	0.25	0.08	3
Colocasia	0.28	0.08	3
Alocasia	0.33	0.11	3
Xanthosoma	2.04	0.21	3

These results (Figure 7.1, Tables 7.1 and 7.2) show that taro starches produced stronger gels than cassava starch at 5% w/w starch concentration.

7.2.4 Discussion

The *Alocasia* and *Colocasia* starch gels had similar strength to that of cassava starch gel, while *Xanthosoma* starch gel showed a significantly higher strength, several times higher than that of all of cassava, *Alocasia* and *Colocasia* starch gels. The strength of the gels increased slightly from cassava to *Colocasia* to Alocasia.

These results are consistent with those obtained from the Brabender amylograph. Upon cooling of the gelatinized starch suspensions to room temperature in the Brabender amylograph test, the gels set to relative viscosities of the same order as that obtained for gel strength tests, ie. *Xanthosoma* starch gel showed the highest viscosity and gel strength, followed by *Alocasia*, *Colocasia* and cassava respectively.

It can also be seen in Figure 7.1 that there are significant differences between the starch gels in terms of their thermoproperties. As the starches were heated over the

temperature gradient of 25 - 90°C, the *Xanthosoma* and cassava starch gels showed a similar degree of loss of shear complex modulus G* values (ΔG^* = 18.5 and 12.7 Pa respectively). The *Alocasia* and *Colocasia* starch gels, on the other hand, showed relatively stable gels on heating, maintaining an almost constant value throughout the heating process. The relative loss of shear complex modulus G* values (ΔG^*) were 3.2 and 4.8 respectively.

It has been pointed out earlier (Chapter 1) that starch gels are composites consisting of swollen granules filling an interpenetrating amylose gel matrix (Miles et al.(a) 1985). Morris (1990) pointed out that starch gels should be discussed in terms of the properties of the gel matrix (amylose), the deformable filler (swollen granules), the volume fraction of filler, and the filler-matrix interaction. Miles et al.(a), (1985) pointed out two distinct phenomena: A short-term development of gel structure and crystallinity, which was found to be dominated by irreversible (T <100°C) gelation and crystallization within the amylose matrix, and a long-term increase in the modulus of the starch gels which were related to a reversible crystallization, involving amylopectin, within the granules on storage. It was also reported that the crystallisation resulted in an increase in the rigidity of the granules and thus enhanced their reinforcement of the amylose matrix.

The relative strength of the taro starch gels could be said to be due mainly to the short-term gelation and crystallisation of the amylose matrix. Miles et al.(b), 1985, has pointed out that the development of the storage shear modulus G' for amylose gel was concentration dependent. Because the *Xanthosoma* starch contained the highest level of amylose, it follows that its gel displayed a relatively high complex shear modulus value G*. The relatively low gel strength of cassava, given its comparatively high amylose content, could not be explained on this basis.

Both of the *Xanthosoma* and cassava starch gels showed a similar loss of complex shear modulus G* during heating over the temperature range of 25 - 90°C. This may be due to some reversible crystallisation of amylopectin during the two hour equilibration time at room temperature of the starch gels before measurement (refer

to Section 3.5.2). This may be related to the size of starch granules. Both of the granules of these starches were relatively large compared to that of both *Colocasia* and *Alocasia*.

7.3 Gel Crystallisation

Crystallisation of starch gels was studied using DSC. The method used for this analysis was that of White et al., 1989. The crystallisation of starch gel is a reversible thermal change, which can be evaluated by using DSC techniques. The amount of energy required to break down crystallised starch gel can be measured as a percentage of the energy required for gelatinization of that starch (White et al., 1989). This method was used to measure the extent of crystallisation of the taro starch gels as they were stored at 5°C and 22°C for 10 days. Table 7.3 summarises the results.

7.3.1 Results

Table 7.3: Crystallisation of starch gels after storage at 5 and 22°C for 10 days measured by DSC.

	Gelatinization[2]			5°C storage					22°C storage			
Starch[1]	Starch Conc.%	T_o	T_p	ΔH_G	T_o	T_p	ΔH_{S5}	% R	T_o	T_p	ΔH_{S22}	% R
Cassava	7	68.8	75.3	0.88	41.3	62.6	0.34	38.4	40.0	59.1	0.20	22.3
	10	69.0	74.6	1.35	40.4	63.1	0.53	39.5	41.0	62.1	0.29	21.4
	20	68.1	74.2	2.73	41.2	62.8	1.10	40.1	40.2	58.0	0.50	18.3
	30	68.2	75.4	3.44	39.6	63.1	1.41	41.0	42.1	62.8	0.73	21.3
*Alocas*ia	7	68.9	80.7	0.63	38.6	61.1	0.26	41.3	36.3	56.6	0.24	38.1
	10	69.3	80.0	1.09	39.7	58.3	0.46	42.4	37.9	57.1	0.40	36.7
	20	69.7	80.9	2.53	36.3	58.8	1.10	43.4	36.8	58.4	0.94	37.1
	30	70.1	80.5	3.11	40.0	60.1	1.40	45.1	41.0	57.0	1.21	38.9
Colocasia	7	79.1	85.5	0.78	39.3	62.4	0.11	36.1	34.3	60.3	0.17	21.2
	10	78.4	84.8	1.20	41.2	59.7	0.14	32.3	38.7	58.7	0.25	20.5
	20	78.4	85.3	2.08	38.0	62.7	0.74	35.4	40.8	61.6	0.51	24.3
	30	78.7	85.0	3.28	42.3	60.1	1.13	34.3	39.3	62.1	0.78	23.7
Xanthosoma	7	74.8	85.6	0.92	40.1	52.1	0.44	48.1	43.2	53.1	0.28	30.1
	10	75.0	85.8	2.03	39.8	61.7	0.93	46.3	39.8	54	0.60	29.3
	20	74.9	85.1	3.12	39.2	58.1	1.58	49.1	41.3	53.6	1.10	34.3
	30	75.2	85.5	4.64	40.1	60.9	2.50	53.8	40.2	54.2	1.61	36.1

1 = each value of T_o, T_p, and ΔH is an average of three measurements
2 = results for gelatinization as summarised in Table 6.4, in chapter 6
T_o and T_p = onset and peak temperatures (°C)
ΔH_G and ΔH_s = enthalpy (J/g) of gelatinization and crystallisation
% R = crystallisation, calculated as percentage of enthalpy of gelatinization, % R = $\Delta H_S/\Delta H_G \times 100\%$

7.3.2 Discussion

White et al., 1989, reported that after storing for four week period at 4°C, 87% of the crystallisation peak of regular maize starch and 91% of waxy maize starch developed during the first week. Only a slight increase was observed thereafter. In was this study it was decided to use a storage time of 10 days. It was assumed that a similar degree of crystallisation might occur in the taro starch gel.

Each of the reported values of T_o, T_p, and ΔH was an average of three measurements. The standard error was between the range of ± 0.5 to 25%, except for few measurements of *Alocasia* where the error was up to 40%. In such cases, the odd values were not included. The measurements for the T_p of the stored gels varied the most. This was basically due to the irregularity in the shapes of the endothermic peaks. The enthalpy measurements, however, had vary little variations.

The results showed that for all starches, the endothermic transition of the recrystallized starch occurred at a considerably lower temperature than that of gelatinization. This was also observed to be true for potato, arrowroot, and other cereal starches by White et al., 1989. Both of the onset and peak temperatures did not appear to depend on the concentration of the starch gels. Unlike the gelatinization temperatures where there was a defined onset temperature for each starch, there were very similar onset temperatures among all the crystallised (retrograded) starch gels. This suggested that a similar type of molecular bonding with similar associative forces developed during crystallisation in all the starch gels. Crystallisation in all the stored starch gels, occurred over a wider range of temperatures (not shown in the table, indicated by T_p - T_o) than that for gelatinization.

The enthalpy of crystallisation (ΔH_S), like the enthalpy of gelatinization (ΔH_G), showed an increase with increasing concentration of starch gels. This observation was to be expected, since the degree of recrystallisation depends on the concentration of molecules that form the gel network (Miles et al., 1984). White et al., 1989, reported that no crystallisation occurred in potato and cereal starch gels with concentration of less than 10%, after storage for 7 days at 4, 21, and 30°C. This

does not appear to be the case with both taro and cassava starches. Crystallisation appeared to take place even for 7% starch gels. Although the enthalpy of crystallisation (ΔH_s) was shown to be depending on gel concentration, expressing this enthalpy as a percentage of enthalpy of gelatinization (% R) did not seem to show dependency on concentration.

Crystallisation of starch gels was relatively larger in starch gels stored at 5°C than that in starch gels stored at 22°C. This observation was reported to be true for other starches by other workers (Miles et al., 1985; Morris, 1990; White et al., 1989).

It can also be seen that the level of crystallisation in stored starches seemed to be following the order of enthalpy of gelatinization for the test starches. It had been pointed out earlier that the test starches followed the order: *Xanthosoma* starch giving the highest enthalpy of gelatinization, followed by cassava, *Colocasia* and *Alocasia* which had similar heat of gelatinization. For example, 30% concentration gels showed 2.50, 1.41, 1.40, and 1.13 J/g enthalpy of crystallisation for *Xanthosoma*, cassava, *Alocasia*, and *Colocasia* starches respectively, on storage at 5°C storage. *Xanthosoma* also exhibited the highest enthalpy of crystallisation. The heat of crystallisation is dependent on the associative forces that bind the starch molecules in a gel. These associative molecular forces depend on the molecular structure of the starches. Because the *Xanthosoma* starch contained high proportion of amylose, it follows that it exhibited a relatively high enthalpy of gelatinization and crystallisation.

Within the starch granules, the amylose molecules form crystalline regions due to association of linear molecules. These associations were considered to be stronger than the association of branched molecules of amylopectin. The higher gelatinization temperature of *Xanthosoma* was attributed to its high amylose content. This phenomenon was also applied to crystallinity of the *Xanthosoma* starch gel. Because of the higher number of amylose molecules that made up the amylose matrix of the gel, there was bound to be larger proportion of linear molecules lying adjacent to each other hence forming stronger bonds between them. Therefore a higher enthalpy of crystallisation was shown.

7.3.3 Gel Clarity

Miles et al.(b) (1985), reported that the development of opacity in amylose gel was related to crystallisation during storage. The test starch gels (5% w/w) were investigated for the development of opacity in the starch gels after storage at 5 and 30°C for 10 days. Photographs of the gels were taken. Figure 7.2 shows two sets of freshly prepared starch gels before storage. Figure 7.3 shows the same sets of starch gels after storage for 10 days at (a) 5°C and (b) 30°C. The starches, in duplicate samples, are organised in the figures (7.2 and 7.3, left to right) as cassava (T), *Xanthosoma* (X), *Colocasia* (C), and *Alocasia* (A).

Comparing the freshly prepared starch gels, cassava starch gel exhibited a superior clarity than all the taro starch gels. This result is consistent with the report of Moorthy et al. (1993). The *Xanthosoma* starch gel, exhibited a relatively clear starch gel similar to that of the cassava starch gel. *Alocasia* gel showed a rather poor clarity with *Colocasia* gel showing a medium clarity.

It was also observed that after storage, opacity developed to a larger extent in gels stored at 5°C, than those stored at 30°C. This result was consistent with the crystallisation test. It can also be seen that opacity was most prominent in *Xanthosoma* starch gel. In Figure 7.3(b), it can be seen that a clear water layer had developed already on top of each of the *Xanthosoma* samples. This indicated a severe syneresis had occurred. This again was consistent with the syneresis tests (Section 7.4).

Figure 7.2: Two sets freshly prepared 5% (w/w) starch gels, before storage at 5°C and 30°C respectively.

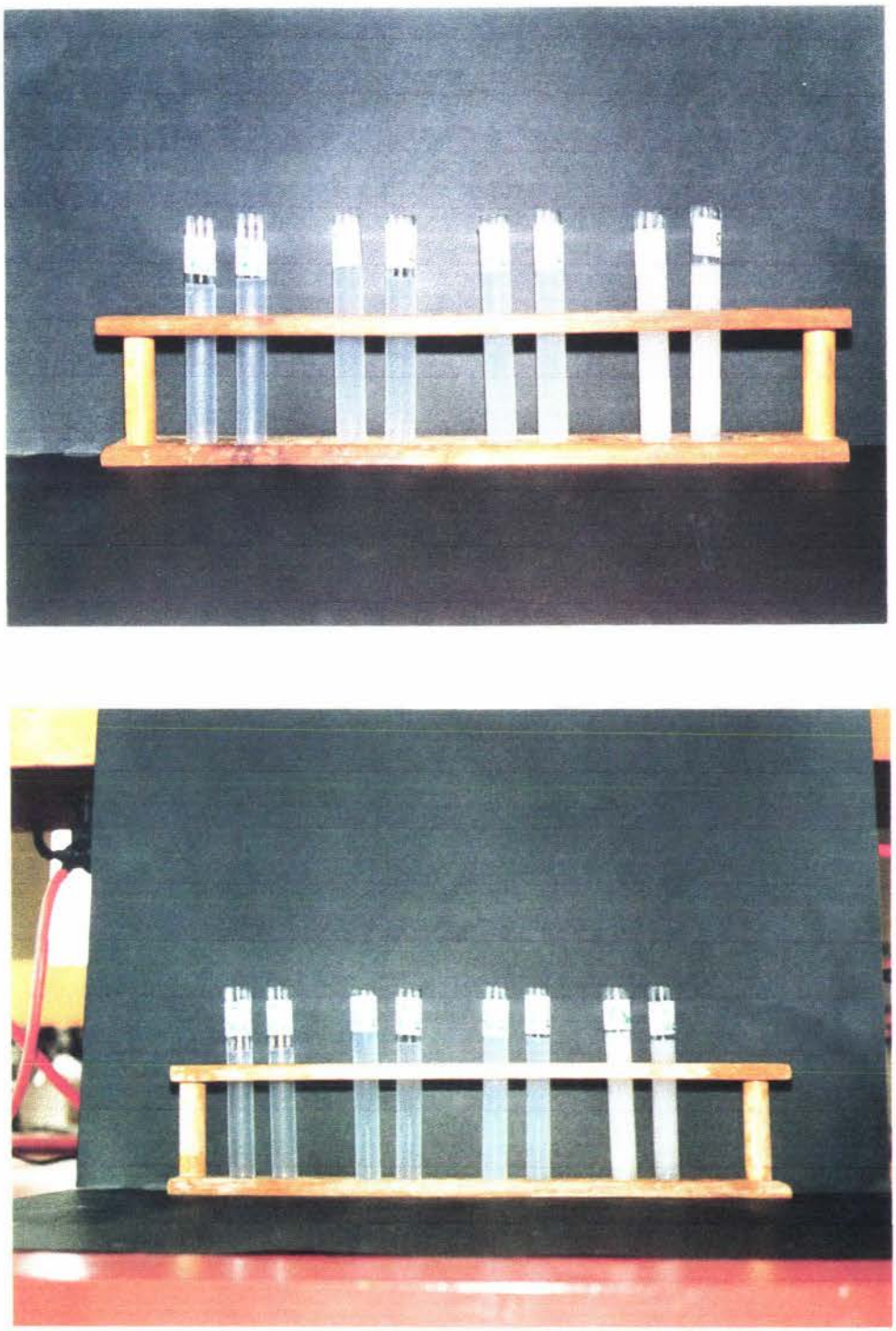
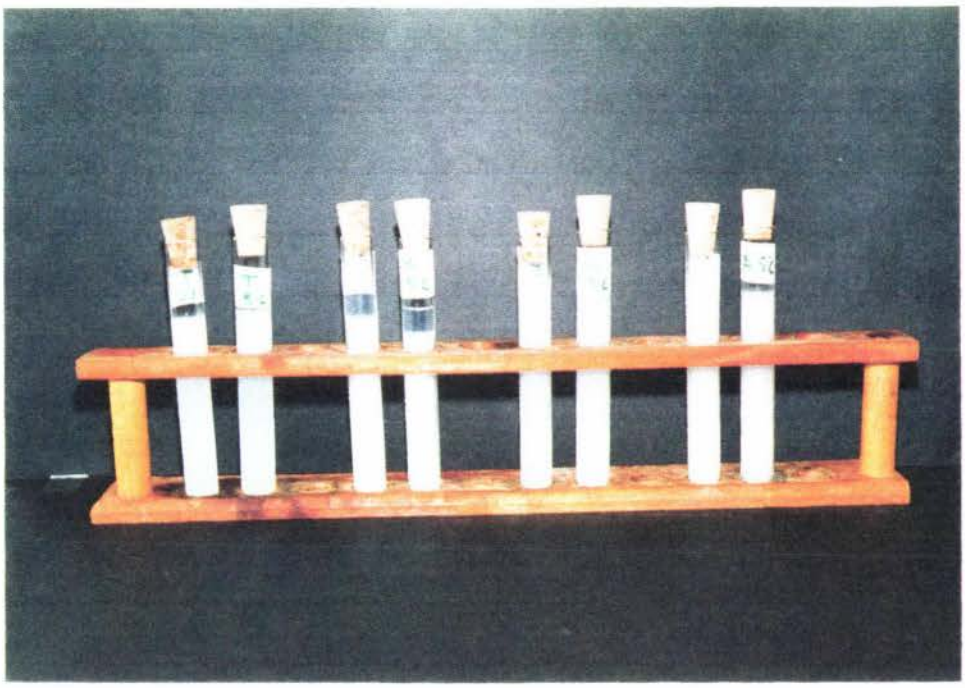
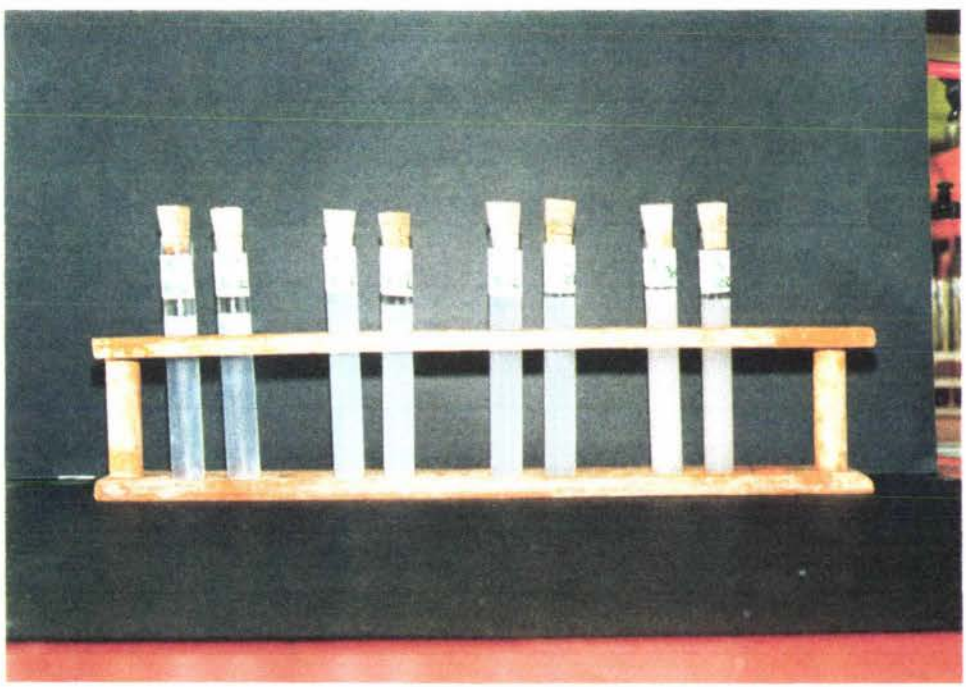


Figure 7.3: Starch gels after storage for 10 days at (a) 5°C, and (b) 30°C

a)



b)



7.4 Syneresis

The starch gels were investigated for their tendency to undergo syneresis. This was carried out by directly measuring the amount water separated from the starch gels after storage at different temperatures for certain periods. After storage, the starch samples were centrifuged, and the water separated was discarded. The samples were weighed and the weights of water separated were expressed as percentages of the original sample weights (See Section 3.6.3 for details of the method). Table 7.4 summarises the results.

7.4.1 Results and Discussion

Table 7.4: Water separated from the starch gels (% Syneresis) after storage

Starch	Storage Time (days)	% Syneresis[1] 5°C	22°C	30°C
Cassava	1	ns	ns	ns
	2	ns	ns	ns
	4	0.2	ns	ns
	8	0.53	0.1	0.2
	12	6.51	6.0	0.9
Alocasia	1	ns	ns	ns
	2	ns	ns	ns
	4	0.3	ns	ns
	8	0.5	ns	ns
	12	1.4	ns	ns
Colocasia	1	ns	ns	ns
	2	ns	ns	ns
	4	2.3	ns	ns
	8	4.1	5.8	ns
	12	6.3	nm	ns
Xanthosoma	1	10.1	ns	ns
	2	20.5	ns	ns
	4	41.3	ns	ns
	8	45.3	1.2	ns
	12	nm	2.3	ns

nm = not measured
ns = no syneresis
1 = average of three replicates

The table shows that the gels were more prone to syneresis when stored at lower temperature and the *Xanthosoma* starch gel showed higher tendency to undergo syneresis than the other starches. These results are in close agreement with the crystallisation test which indicated that the *Xanthosoma* gel was highly prone to crystallisation.

7.5 Freeze-Thaw Stability of Taro Starch Gels

Freeze-thaw stability of starch gels is a very important characteristic for many food applications. The ability of a starch gel to maintain its functional properties during freeze-thaw treatment is a desirable characteristic that is required in many food applications. Several techniques were employed to investigate the freeze-thaw stability of the taro starch gels.

7.5.1 Thermoproperties of Freeze-Thawed Taro Starch Gels

Introduction

The thermoproperties of the starch gels were tested by determining the changes that occurred in the rheological properties of the gels during heating over a temperature gradient of 25 to 90°C. The changes in the rheological parameters (G*, G' and G") were followed in the oscillation mode in a Bohlin VOR Rheometer. The test starch gels were subjected to repeated freeze-thaw (FT) cycles, transferred to the sample cup, and then tested in the same way and conditions as described in Section 3.6.1. Only the changes in the complex shear modulus G* are presented, for conciseness.

For each starch gel, three points of interest were recorded:

- The value of G* at 26°C (G^*_{26}), for each FT cycle. This value would reveal information about the initial strength or rigidity of the thawed gel. In some of the runs there seemed to exist some noise in the first one or two measurements (eg. 3rd. FT cycle for *Alocasia* and *Colocasia* starch gels), so the values at 26°C were used, where graphs appeared to be more steady.

- The value of G* at 90°C (G^*_{90}). This data would give information on the final strength or rigidity of each thawed starch gel at the end of the heating process.
- Initial melting temperature (T_i). Temperatures at which G* started to drop in values. This was considered to be the temperature at which the crystallinity of each thawed starch gel started to melt

Results and Discussion

Effect of Freeze-Thaw Treatment on Complex Shear Modulus G*

The effects of freeze-thaw treatment on the test starch gels, as followed by the changes in the complex shear modulus G* are shown in Figures 7.4, 7.5, 7.6, 7.7, for *Xanthosoma, Alocasia, Colocasia*, and cassava starch gels respectively.

Figure 7.4: Effect of Freeze-Thaw Treatment on 5% Xanthosoma Starch Gel

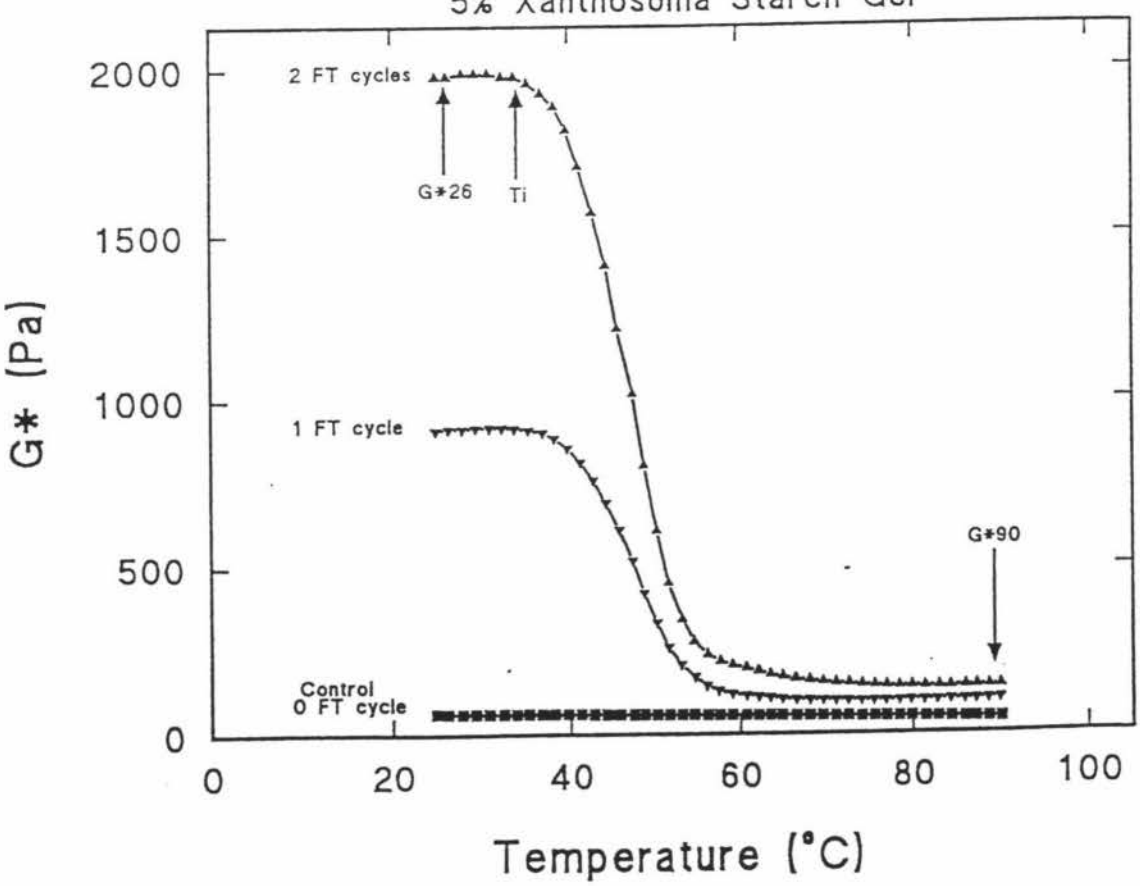


Figure 7.5: Effect of Freeze-Thaw Treatment on 5% Alocasia Starch Gel

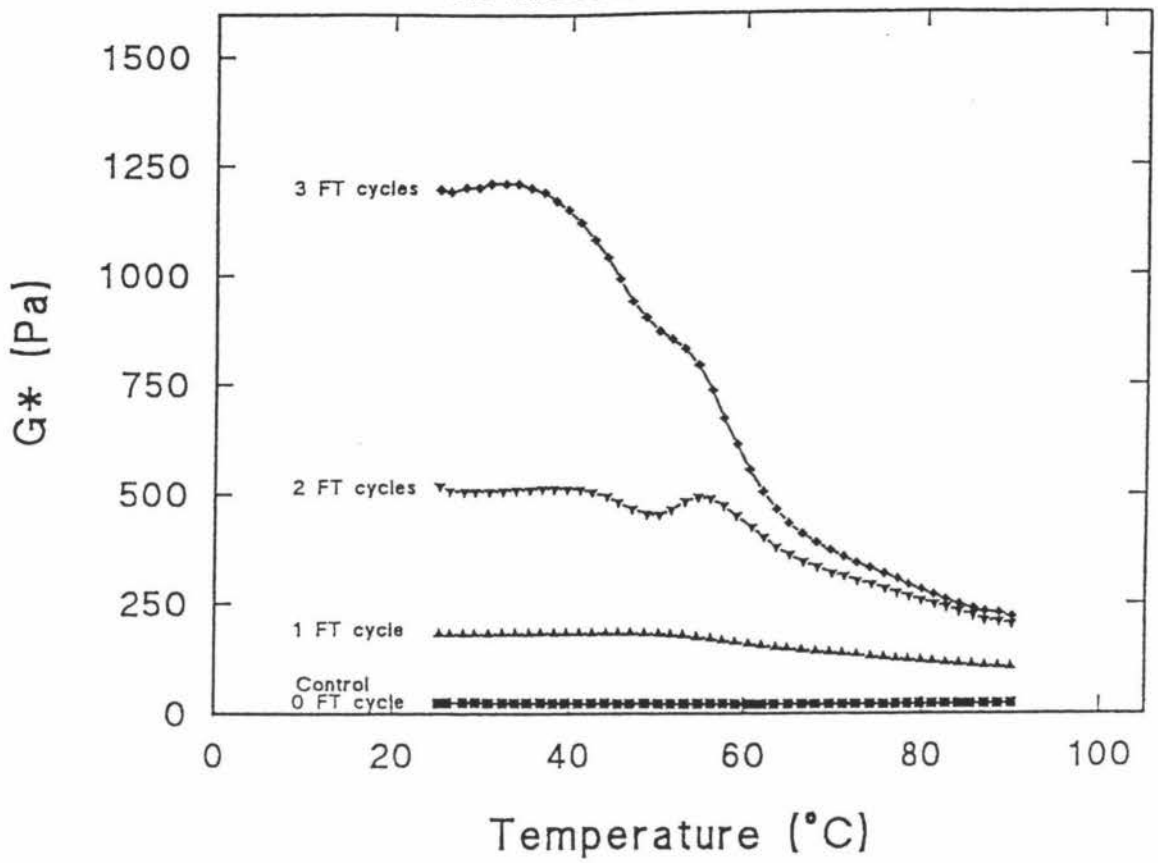


Figure 7.6: Effect of Freeze-Thaw Treatment on 5% Colocasia Starch Gel

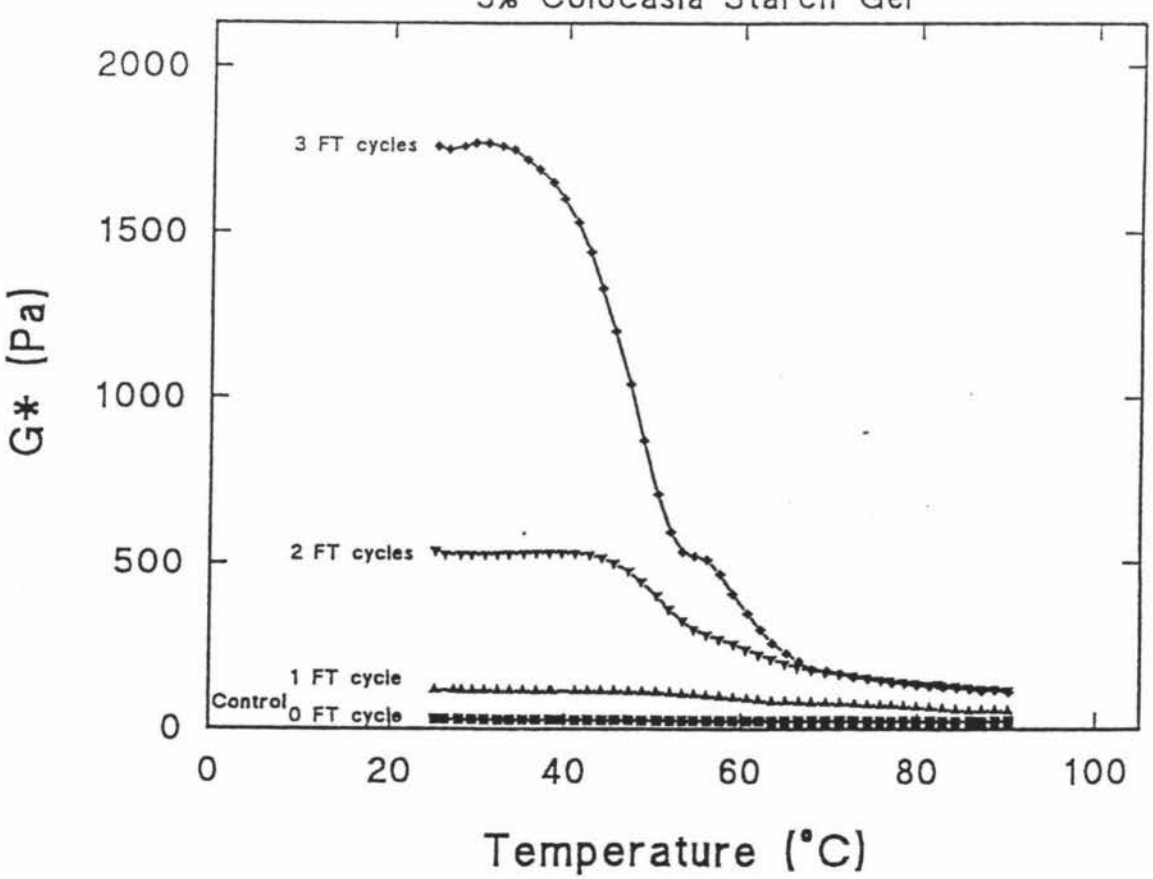


Figure 7.7: Effect of Freeze–Thaw Treatment on 5% Cassava Starch Gel

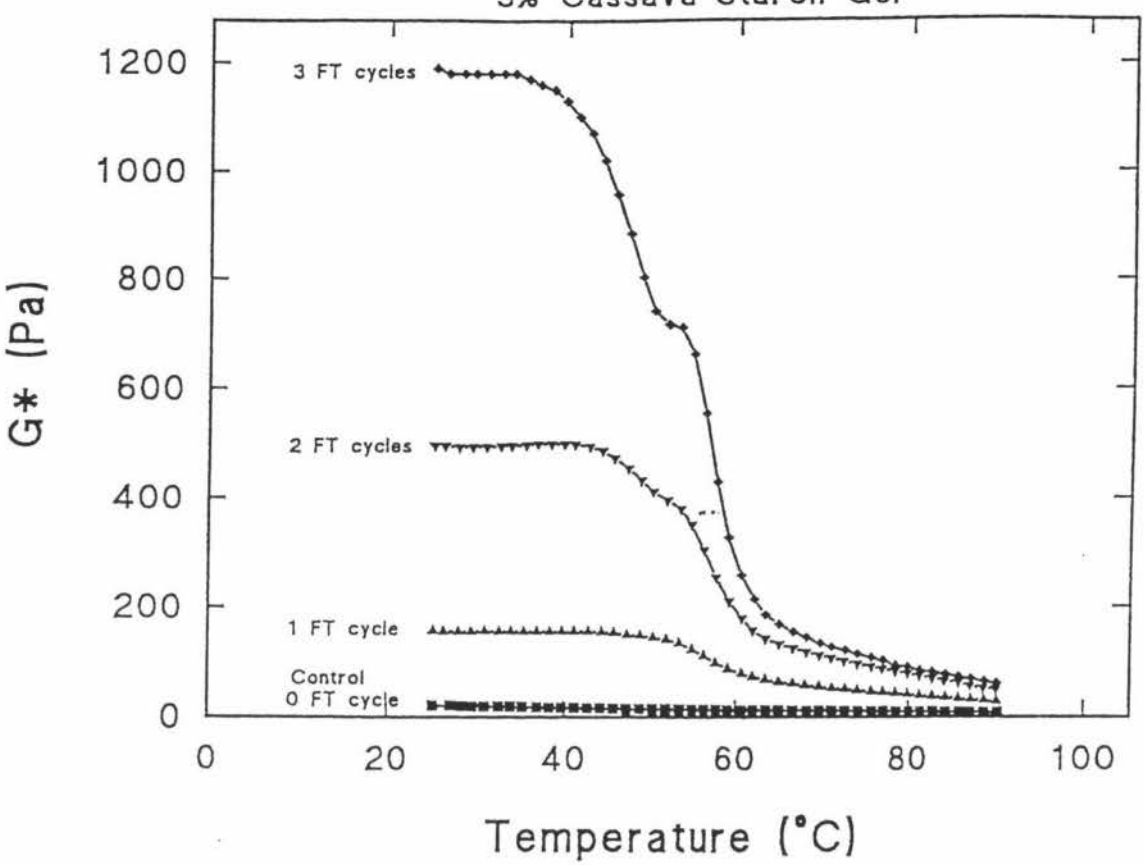


Table 7.5 summarises the recorded points of interest for each measurement.

Table 7.5: Effect of freeze-thaw treatment on starch gels

FT cycle	Reference Point	Cassava	*Alocasia*	*Colocasia*	*Xanthosoma*
0	G^*_{26} (Pa)	20	25	29	62
	G^*_{90} (Pa)	8	23	24	44
	T_i (°C)	-	-	-	-
1	G^*_{26} (Pa)	155	180	117	915
	G^*_{90} (Pa)	28	104	55	100
	T_i (°C)	44	50	45	38
2	G^*_{26} (Pa)	493	507	527	1980
	G^*_{90} (Pa)	49	202	116	139
	T_i (°C)	39	40	39	38
3	G^*_{26} (Pa)	1190	1200	1750	-
	G^*_{90} (Pa)	60	218	116	-
	T_i (°C)	38	38	38	-

Comparing the starch gels before freeze-thaw treatment (0 FT, Table 7.4), showed relative gel strength of the same order as that discussed in Section 7.2.3, ie. *Xanthosoma* starch gel showed highest gel strength, followed by *Colocasia*, *Alocasia* and then cassava starch gels. The *Xanthosoma* and cassava starch gels showed a relatively larger decrease in G* after heating from 25 to 90°C, compared to *Alocasia* and *Colocasia* starch gels.

After 1 FT cycle, the values of G^*_{26} for all the starches increased to many times their values (up to 15 times for *Xanthosoma* starch gel) before any freeze-thaw treatment was carried out. These increases were due mainly to high level of recrystallisation of starch molecules developed during the freeze-thaw treatment. The relatively high G^*_{26} value (915 Pa) for *Xanthosoma* starch gel indicate that this starch is extremely susceptible to retrogradation compared to other starch gels. The cassava and *Alocasia* starch gels showed similar increases in G^*_{26} (155 & 180 Pa respectively), after 1 FT cycle, while *Colocasia* gel showed an increase to a smaller value (117 Pa).

After 2 FT cycles, *Xanthosoma* gel again exhibited a comparatively high G^*_{26} value (1980 Pa), more than double its value after 1 FT cycle. It was not analyzed for 3 FT cycles because the gel became so stiff, and no longer exhibited the viscoelastic properties, ie. it was more like a solid than a gel. For the other starch gels, the increase in G^*_{26} values were 4 to 5 times their values after 1 FT cycle. They all exhibited similar G^*_{26} values after 2 FT cycle, (507 Pa, *Alocasia*; 527 Pa, *Colocasia*; and 493 Pa, cassava). These values were still lower than the value for *Xanthosoma* starch gel after 1 FT cycle (915 Pa), again showing extreme *Xanthosoma's* susceptibility to crystallisation.

After 3 FT cycles, the *Alocasia* and cassava starch gels showed similar increases in G^*_{26} (1200 and 1190 pa respectively), while *Colocasia* increased to a higher value (1750 Pa). Comparing the four starch gels it can be concluded that the *Xanthosoma* starch gel is extremely susceptible to retrogradation, Cassava and *Alocasia* starch gels are similarly susceptible to retrogradation to a relatively less degree, *Colocasia* gel is susceptible to a medium degree.

Effect of Freeze-Thaw Treatment on T_i

At the initial stage of heating/measurement, the thawed starch gels exhibited high initial values of G*. These high initial values corresponded to a high degree of crystallinity and stiffness of the gels due to a high number of intermolecular bonds formed during the freeze-thaw treatment and storage of the gels. Upon heating to a certain temperature, T_i, G* started to drop. This drop is suggested to correspond to the "melting" or breaking of these inter-molecular bonds.

The temperature (T_i) at which G* started to drop decreased with increasing number of FT cycles. It might be more appropriate to say that the initial melting temperature (T_i) of freeze-thaw treated starch gels decreased with increasing degree of crystallinity and stiffness of the gel.

After 1 FT cycle, the T_i for *Alocasia*, *Colocasia* and cassava gels were 50, 45, and 44°C respectively. These temperatures corresponded to G* values of about 500 Pa. T_i dropped to 38°C after 3 FT cycles in all these gels with correspondingly high G* values. For *Xanthosoma* starch however, T_i was 38°C corresponding to a G* value of 915 Pa, and T_i decreased further to 37°C after 2 FT for *Xanthosoma* gel.

These changes in T_i can be described in terms of the associative forces that bind the molecules within a gel during crystallisation. It seemed that stronger crystallinity and bonding were formed at the early stage of storage and freeze-thaw treatment, and relatively weaker bonds developed thereafter. The stronger (primary) bonds may be formed between linear molecules or portions of molecules aligning closely parallel to each other within the gel. The formation of these bonds may lead to formation of relatively weaker (secondary) bonds between portions of molecules which might have been brought closer together as a result of the primary bonds being formed. These bonds seemed to develop at the later stage of storage or freeze-thaw treatment.

Upon heating, the secondary bonds, because of weaker intermolecular binding forces, started to melt first, showing an early drop in G* (38°C, after 3 FT cycles). Further heating continued to melt the primary bonds which corresponded to the later stage of the melting phase. It seemed that the primary bonds dominated the crystallisation

after the first FT cycle, hence the T_i was relatively high (45 - 50°C see Table 7.4). The secondary bonds seemed to be more prominent after 3 FT cycles showing an earlier melting temperature , T_i (38°C).

Figures 7.5, 7.6, 7.7 show a peak developed in modulus G* after 2 & 3 FT cycles, at around 50 to 60°C. The *Xanthosoma* starch gel did not exhibit a peak. Eliasson and Kim (1992) reported the development of the same peak in the complex modulus G* for hydroxyl potato starch gel after 6 FT cycles. The magnitude of this peak was reported to be increasing with the number of FT cycles. They also reported that the appearance of a peak in G* during heating of freeze-thaw starch pastes and the magnitude of this peak correlated well with onset and extent of Syneresis. In this study, the peak appeared after 2 FT cycles, in *Alocasia, Colocasia*, and cassava starch pastes. Because raw unmodified starches were used in this study an early appearance of this peak was to be expected. The syneresis test showed that the onset of syneresis occurred even after 1 FT cycle for these starches. Furthermore, this peak did not appear when heating freeze-thawed *Xanthosoma* starch paste, but syneresis was comparatively high even after the first FT cycle. It may therefore be more appropriate to describe this peak in terms of some other mechanism. It seemed that there might be some degree of recrystallization and reassociation of the melted molecules at certain levels of heating. The melting of retrograded starch might result in redistribution of molecules to form a more homogenous matrix where overlapping molecules are rebound showing a peak in modulus G*. These findings need more investigation.

Effect of Freeze-Thaw Treatment on G^*_{90}

It can be seen (Figures 7.4 - 7.7) that for a range of temperatures, 70 - 90°C, there were very little changes in the values of G*. The figures also indicated that the level of G* at this region was progressively increasing with number of FT cycles, up to a point where it did not seem to increase further. In the case of *Colocasia, Alocasia* and cassava G* reached this level after 2 FT cycles.

It was mentioned earlier that starch are composites containing gelatinized granules embedded in an amylose matrix. Miles et al. (a) (1985) described the gelation

process by means of two phenomena: firstly, a short-term development of gel structure and crystallinity dominated by irreversible (T <100°C) gelation and crystallisation within the amylose matrix. This was referred to as phase separation into polymer-rich and polymer-deficient regions. Secondly, a long-term increases in the modulus of the starch linking to a reversible crystallisation, involving amylopectin, within the granules during storage.

It was considered that the initial modulus of the thawed starch pastes (indicated by G^*_{26}) corresponded to the long-term reversible crystallisation involving amylopectin. The final modulus of the paste after heating, G^*_{90} corresponded to the irreversible gelation and crystallisation within the amylose matrix. Heating from 70 to 90°C did not seem to melt the pastes. Given these considerations, this method could be used to give a measure of how much retrogradation corresponded to amylose or amylopectin crystallisation at any stage of storage (FT cycles).

Taking *Colocasia* paste for example (Table 7.4), the paste reached a constant final G^*_{90} of 116 Pa. after the 2nd. FT cycle. The freshly prepared paste exhibited a modulus G^*_{26} of 29 Pa. After 1 FT cycle, G^*_{26} of the same paste went up to 117 Pa, and on heating to 90°C, this value went down to 55 Pa (G^*_{90}). The total retrogradation therefore, is given by (117 - 29) Pa. Retrogradation due to amylose crystallisation after 1 FT cycle is given by (55 - 29) Pa.

The results also showed that the initial structure and texture of a frozen gel could never be fully recovered, even on heating to 90°C. ie. the value of G^*_{90} will never reach down to the initial G^*_{26} of the freshly prepared paste. The value of G^*_{90} could be used as an indication of the texture recovery of freeze-thaw starch pastes. This measure can be used in determining the suitability, or otherwise, of different starch pastes for food products which are subjected to freeze-thaw treatment.

Effect of Storage Time

The effect of storage was followed by measuring the complex modulus G* of samples stored at -10 and 22°C for various storage times. Figures 7.8, 7.9, 7.10, 7.11, show the effect of various storage times on G* for *Xanthosoma, Alocasia, Colocasia*, and cassava starch pastes at both temperatures. It can be seen that there was very little development of G* during storage at 22°C for 3 days, the graphs of G* showed very little change.

Figure 7.8: 5% Xanthosoma Starch Gel
Effect of Storage Time

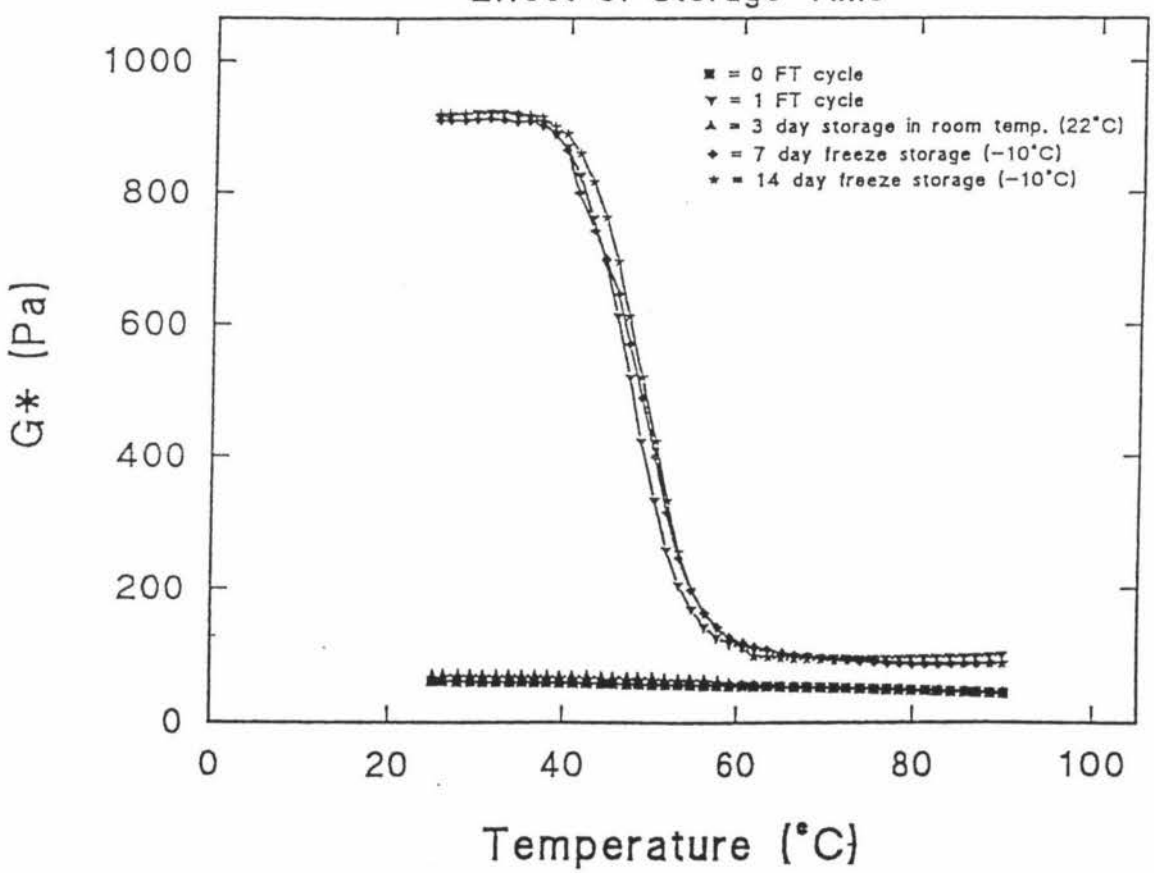


Figure 7.9: 5% Alocasia Starch Gel
Effect of Storage Time

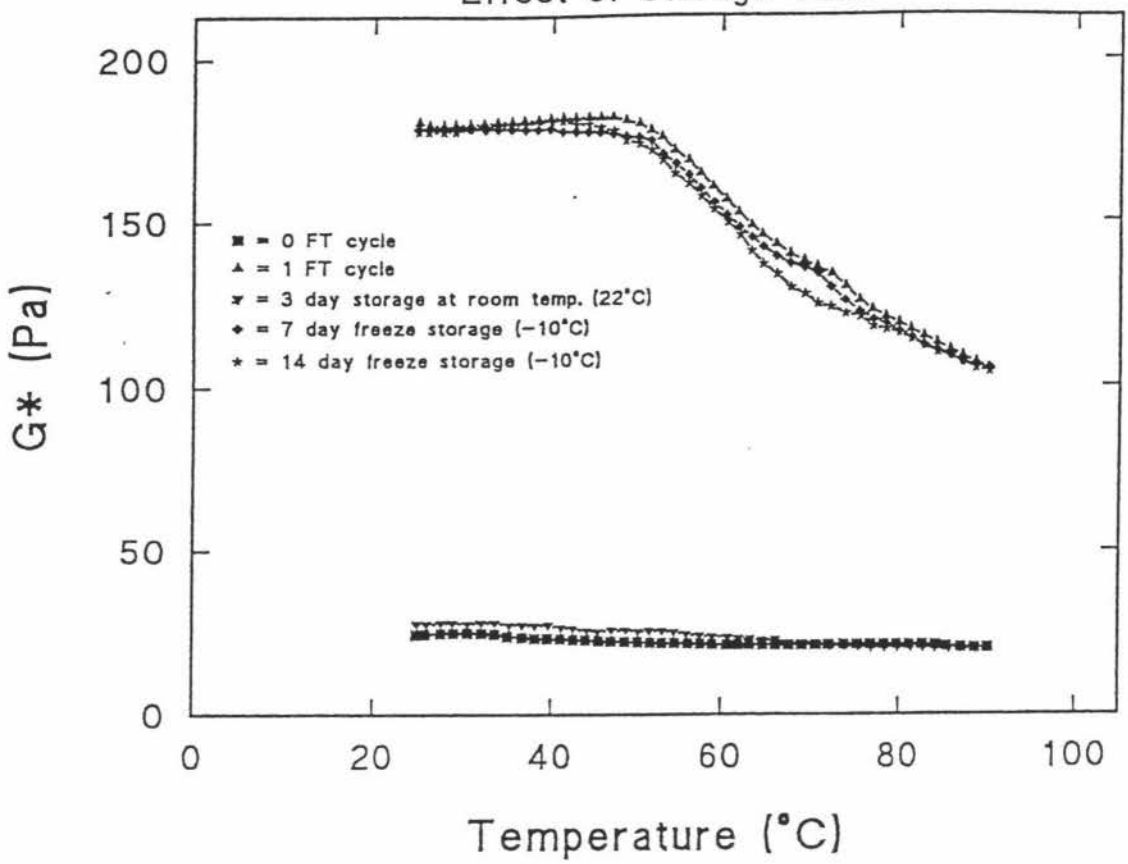


Figure 7.10: 5% Colocasia Starch Gel
Effect of Storage Time

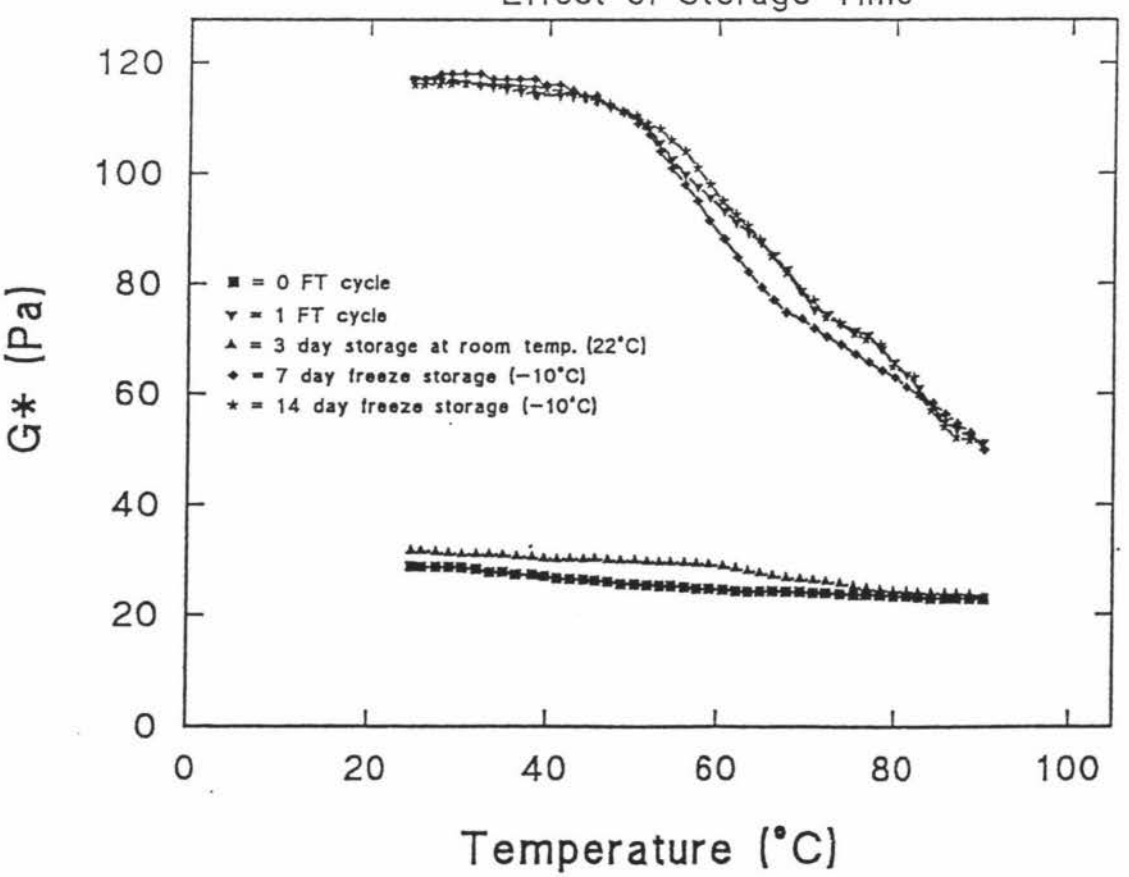
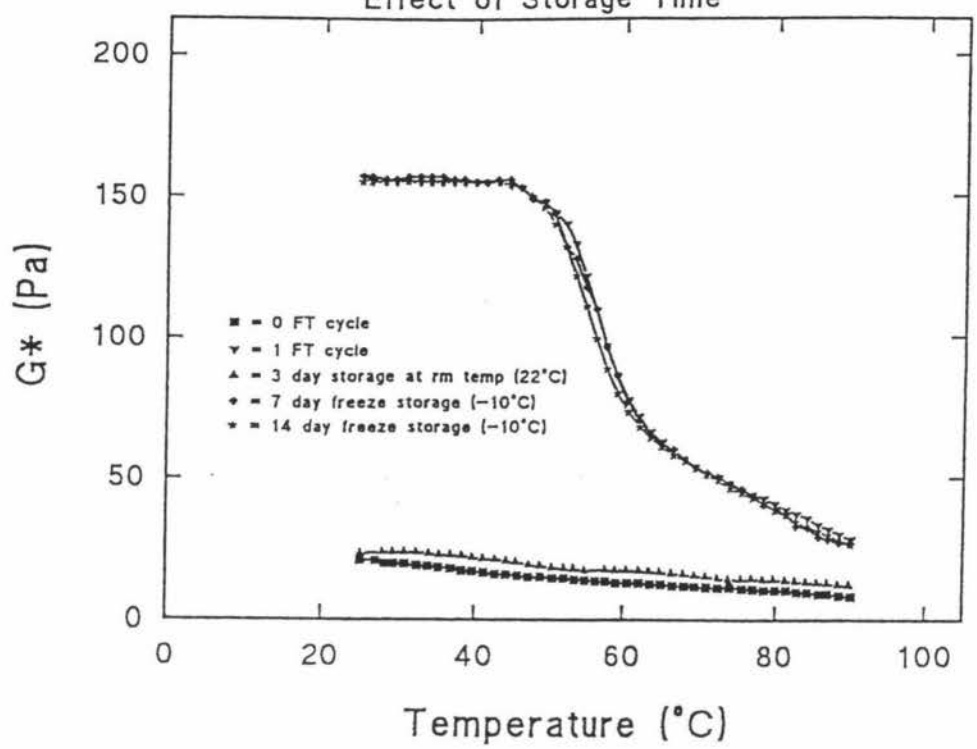


Figure 7.11: 5% Cassava Starch Paste
Effect of Storage Time



There was insignificant differences in the modulus G* after storage, for all the test gels, for 7 and 14 days at -10°C. Heating the thawed gels from 25 to 90°C, they all exhibited a modulus G* patterns that were very similar to that of their 1 FT cycle G* patterns. These results show that retrogradation occurred when the samples were undergoing freezing or thawing rather than during freezing. On freezing a gel, starch molecules may promote nucleation of ice crystals. Once the nucleation has occurred, the ice crystals increase in size. The water molecules diffuse towards these crystals enforcing the phase separation process hence increasing the crystallisation of starch molecules. These processes are most prominent at low freezing rates. Once all the gel network is frozen, there is no more crystallisation. Because 1 FT treatment and freeze storing for various lengths of time involved freezing once, their effect on the modulus G* of the gels was the same.

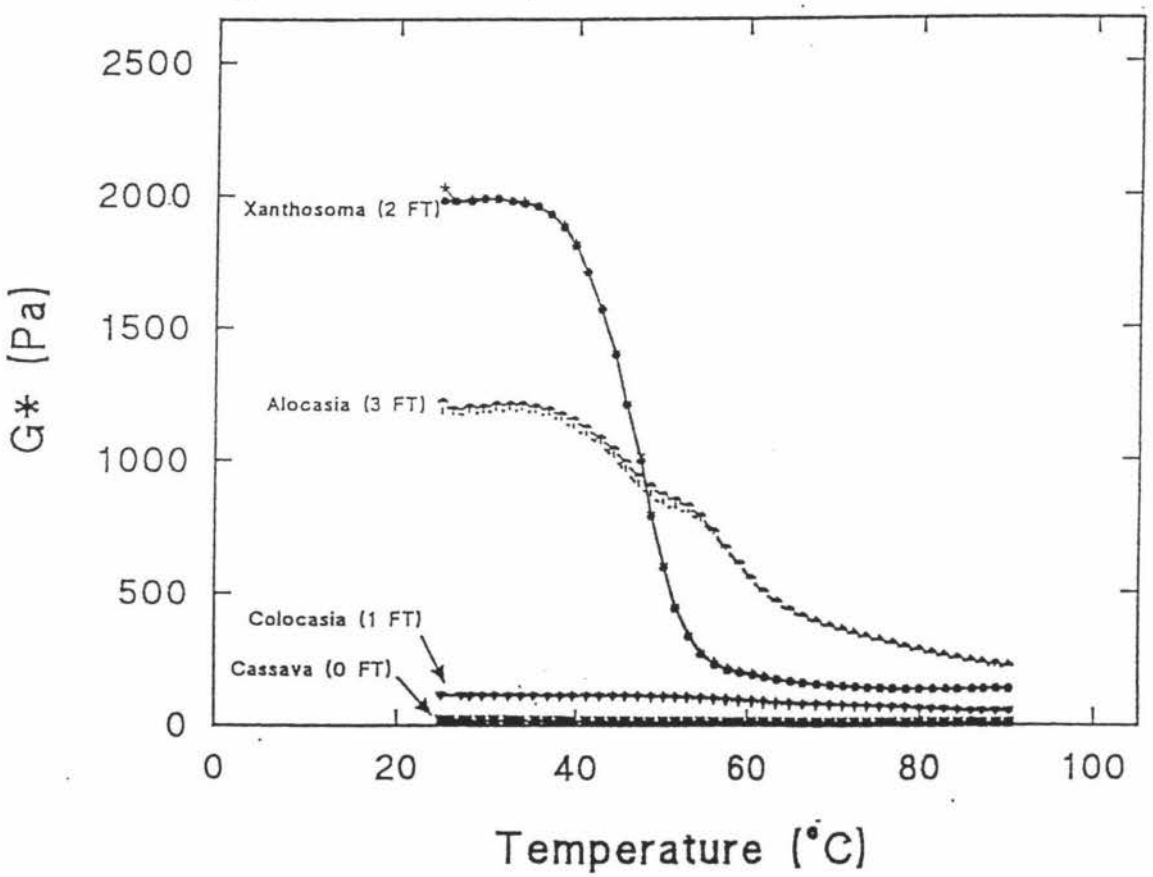
Experimental Error of Rheological Measurement

The experimental error in rheological measurements was continuously monitored during measurement of each FT cycle by replicate runs of each sample. Several samples showing significant variations between the replicates were tested further by

testing more replicates of the same samples until repetitive results were obtained. Figure 7.12 presents typical replicate runs for various samples. Note that each curve consists of duplicate runs of the same sample subjected to the same treatment.

It was found that the rheological measurement was sensitive to small changes in sample size, and conditions. Small variations in the size of the samples showed significant variations in the measured G* modulus of the gels. The transferring of samples from the freezing containers to the measuring cup often subjected the samples to mechanical deformation and fracture before measurements commenced. This deformation also significantly altered the rheological measurements.

Figure 7.12: Sample Rheological Measurement Error



It was therefore a very important consideration in this rheological measurement that when transferring the samples to the measuring cup, disturbance of the gel structure be minimal. The ideal situations would be to freeze the samples in the measuring cup. This would eliminate the need to transfer the samples from one container to another. Unfortunately, there was only one measuring cup available, so freezing of

samples had to be carried out using other containers. The sample size was kept constant for all samples using a volumetric cylinder for measuring the gel samples.

Rheological Measurement Conditions

In this study, only one set of measurement conditions was used (Section 3.6.1). There were various parameters that could be altered in order to optimise measurement of various gels or viscoelastic materials. The use of the 40 g torsion bar, for example, was considered to be suitable for rheological measurement of 5% starch gels. However, it may not be suitable for rheological measurement of 3% starch gel or a 20% starch gel. A larger bar may be needed for rheological measurement of stronger gel, and a smaller bar for a weaker gel. Because of the sensitivity of the measurement, it might be more appropriate to analyze rheological behaviour using a weaker gel (eg. 2-3% concentration). However, using such a low concentration, the starch gel is vulnerable to spontaneous precipitation rather than recrystallisation. Rheological measurement would therefore be misleading. It was not attempted in this study to optimise the measuring conditions for various starch concentrations.

7.5.2 Tensile and Penetration Strength of Starch Gels

An attempt was also made to describe the freeze-thaw properties of the test starches in terms of their rigidity as measured by the penetrating and tensile strengths. The penetrating strength was defined as the maximum force (N) required to penetrate through the starch gel. The tensile strength was defined as the maximum force required to break a gel ring. The penetrating force was measured using the same method as described in Section 3.6.2. Starch gels were subjected to repeated FT cycles. After each FT cycle, three samples of each gel were measured for penetrating strength. The average of the three measurements was recorded as the penetrating strength of the starch gels.

The tensile strength of the gels was determined by measuring the fracture strength of gel rings using the method described in Section 3.6.2. The starch gels were subjected to repeated FT cycles in ring moulds. After each FT cycle, the gel rings

were elongated by Instron until they fractured, and the maximum forces at fracture were recorded.

Penetrating Strength

Table 7.6 shows the penetrating force of the test starch gels after each FT cycle. Table 7.7 shows the effect of storage time on the penetrating strength of the starch gels.

Table 7.6: Penetrating Strength of Freeze-Thaw Treated Taro Starch Gels

FT Cycle		0	1	2	3	4
			Force (N)			
Cassava		0.25	0.94	2.12	2.51	5.96
	s.d.	0.01	0.04	0.04	0.11	0.26
Alocasia		0.33	0.64	1.06	1.87	4.09
	s.d.	0.11	0.05	0.03	0.14	0.21
Colocasia		0.26	0.57	2.17	5.64	4.34
	s.d.	0.03	0.01	0.10	0.27	0.41
Xanthosoma		2.04	6.90	10.10	12.11	14.66
	s.d.	0.21	0.35	0.28	0.41	0.38

Table 7.7: Effect of Storage Time on Penetrating Strength of Starch Gels

Storage Time	Starch	Cassava	*Alocasia*	*Colocasia*	*Xanthosoma*
Freeze Storage	**3 days**	0.81	1.07	1.75	10.22
	s.d.	0.03	0.01	0.25	2.18
	7 days	0.68	2.55	1.16	8.61
	s.d.	0.04	0.41	0.22	1.63
Room Temp. storage 22°C	**3 days**	0.42	1.01	1.06	2.29
	s.d.	0.11	0.06	0.07	0.52
	7 days	0.13	0.61	1.09	2.32
	s.d.	0.07	0.02	0.10	0.07

It can be seen (Table 7.5) that for all the test starches, the gels exhibited an increasing strength with increasing number of FT cycles. These results were consistent with the results for rheological measurements for thermoproperties of the gels (Section 7.5.1). It was shown that the initial modulus of a freeze-thawed starch gel (G^*_{26}) increased with increasing number of FT cycles. It was also suggested that this increase was attributed to the increasing degree of crystallisation as a result of the freeze-thaw treatment. The results for the penetration tests had proved this suggestion to be true. The increasing crystallisation of the gels with increasing freeze-thaw treatment also increased the rigidity of the gels, resulting in higher force being required to break through the gels during penetration tests.

Xanthosoma starch gel was shown to exhibit the highest force. This result again showed *Xanthosoma* starch was extremely prone to retrogradation. Other starch gels exhibited similar strengths. Because of the relatively high amylose content of *Xanthosoma* starch it exhibited a higher crystallinity and retrogradation. The effect of freeze storage time appeared to be similar to the effect of 1 FT cycle which is consistent with what was demonstrated in the rheological measurements in the thermoproperties (Section 7.5.1).

Tensile Strength

The method attempted to measure the tensile strength of starch gels was that of Kohyama et al. (1993). In this method the test material was in the form of a ring which was prepared using a ring mould. The ring was hung on two L-shaped bars steel bars arranged vertically and elongated by the Instron at a predetermined rate of 3 mm/s. The breaking stress and strain were calculated according to the described method (Kohyama et al. 1993).

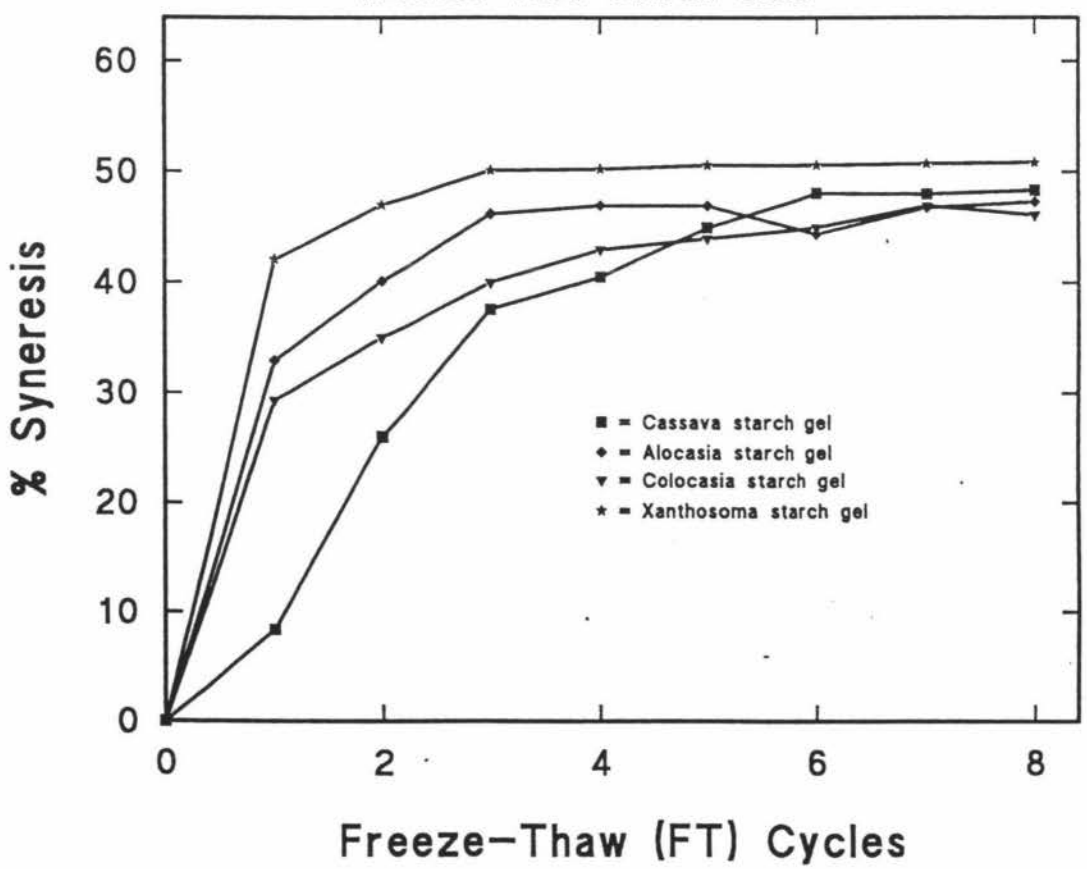
The results showed significant errors between replicates, up to 300% in many cases. Many of the gel rings were too weak, exhibiting inconsistent dimensions. When hung on the steel bar, some gel rings were deformed and partially or fully broken by their own weights, resulting in high variations in measured break stress of replicate samples. It was therefore considered that the attempt to measure the tensile strength

of the gels using this method was unsuccessful. It was found that the gels were a bit heavy and that they were broken by their own weight. Improvement of the method could have been achieved by a) using a gel of higher concentration (eg. 15% w/w), and b) changing the dimensions of the rings. These improvements however were not pursued.

7.5.3 Syneresis

The taro starch gels were also analyzed for their tendency to undergo syneresis. The starch gels were subjected to repeated FT cycles, and then centrifuged. The weight of the separated water was expressed as percentage syneresis, of the initial sample weight. Figure 7.13 shows a plot of syneresis as a function of the number of FT cycles.

Figure 7:13: % Syneresis of Freeze–Thaw Treated Taro Starch Gels



The results showed that all the taro starch gels exhibited significantly higher syneresis than cassava starch gel after 1 FT cycle, *Xanthosoma* 42%, *Alocasia* 33%, *Colocasia* 29%, and cassava 8%. The exhibition of significant syneresis after 1 FT cycle in the taro starch gels did not appear to correlate with the rheological measurements above. It was shown that significantly higher crystallisation (G^*_{26}) occurred after 2 and 3 FT cycles than after 1 FT cycle. Syneresis occurs simultaneously with crystallization. The crystallisation of starch molecules results in separation of water molecules.

The syneresis test of this kind is affected by the centrifugal force used. There seemed to be some alteration of starch gel structure that resulted in partial separation and loosely held water molecules that are separated by centrifugal force, hence significant amounts of syneresis were observed in the gels after 1 FT cycle.

The *Xanthosoma* starch gel exhibited the highest level of syneresis, again indicating its highest vulnerability to retrogradation. Both *Xanthosoma* and *Alocasia* starch gels reached maximum level of syneresis after 3 FT cycles, and there was no further increase with further FT treatment. The *Colocasia* and cassava gels showed a continued increasing syneresis up to a maximum at 5 FT cycles. All the cassava, *Alocasia*, and *Colocasia* gels exhibited a similar maximum syneresis with *Xanthosoma* gel exhibiting a higher maximum syneresis.

7.5.4 Gel Crystallisation

Crystallisation of freeze-thaw treated starch was measured using DSC. Table 7.8 presents T_o, T_p and ΔH for each starch gel after freeze-thaw treatment. Crystallisation was calculated in the same way as that used in Section 7.3. Figure 7.14 presents a plot of percentage crystallisation as a function of FT cycles.

Figure 7.14: Crystallisation of Freeze–Thaw Treated Starch Gels

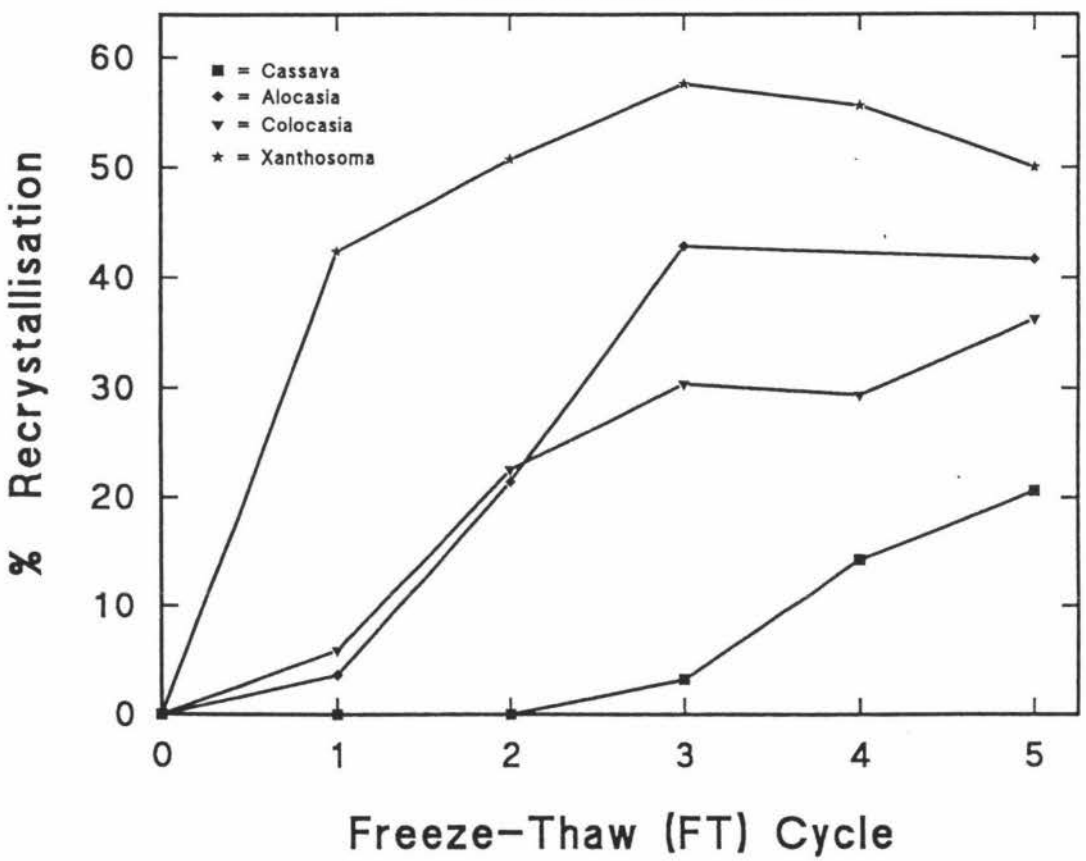


Table 7.8: Crystallisation of freeze-thaw treated starch gels

Starch		FT Cycles 0[1]	1	2	3	4	5
Cassava	**T_o (°C)**	70.3	np	np	64.3	64.2	66.3
	s.d.	0.33	-	-	1.69	0.13	1.71
	T_p (°C)	79.8	-	-	73.8	73.5	77.1
	s.d.	1.10	-	-	2.16	2.01	0.91
	ΔH (J/g)	1.26	-	-	0.04	0.18	0.26
	s.d.	0.01	-	-	0.01	0.01	0.01
	% R	-	-	-	3.2	14.3	20.6
Alocasia	**T_o (°C)**	70.1	60.7	61.9	60.7	58.6	62.6
	s.d.	0.33	1.12	1.30	0.71	2.66	1.36
	T_p (°C)	80.8	69.1	71.4	70.0	67.2	71.5
	s.d.	0.91	0.88	1.52	0.87	1.22	0.73
	ΔH (J/g)	0.84	0.03	0.18	0.36	0.23	0.35
	s.d.	0.07	0.01	0.02	0.01	0.10	0.01
	% R -	3.6	21.4	42.9	27.4	41.7	
Colocasia							
	T_o (°C)	76.1	65.1	62.5	61.4	59.7	64.9
	s.d.	2.41	1.01	0.91	1.06	0.65	1.00
	T_p (°C)	85.5	74.4	70.9	72.1	68.3	72.8
	s.d.	1.66	1.43	1.08	2.11	1.04	2.11
	ΔH (J/g)	1.02	0.06	0.23	0.31	0.30	0.37
	s.d.	0.33	0.01	0.04	0.11	0.07	0.01
	% R	-	5.9	22.5	30.4	29.4	36.3
Xanthosoma	**T_o (°C)**	75.6	61.8	59.9	60.3	60.1	59.4
	s.d.	0.01	1.22	2.08	1.05	0.91	1.22
	T_p (°C)	86.7	68.2	65.8	65.9	67.9	65.6
	s.d.	1.55	1.11	0.88	2.05	0.68	1.51
	ΔH (J/g)	1.44	0.61	0.73	0.83	0.80	0.72
	s.d.	0.01	0.01	0.02	0.33	0.01	0.06
	% R	-	42.4	50.7	57.6	55.6	50.0

1 = average of 15 samples (gelatinization)
s.d. = standard deviation
% R = percentage crystallisation
np = no peak shown
T_o, T_p = onset and peak temperatures
ΔH = enthalpy

The *Xanthosoma* gel exhibited a relatively high crystallisation after 1 FT cycle. This result was consistent with the results for syneresis. It appeared that the crystallisation dropped for the 4th and 5th cycles. This could be due to an unidentified factor. The *Alocasia* and *Colocasia* gels exhibited a very similar crystallisation at 1 and 2 FT cycles. The cassava starch showed no crystallisation after 1 and 2 FT cycles. This is not consistent with the syneresis tests where there was syneresis detected even after the first FT cycle. Although there were discrepancies with this set of data, it appear that starch gels followed a very similar pattern as that for syneresis, ie. *Xanthosoma* gel showing the highest for crystallisation, *Colocasia* and *Alocasia* gels appeared to have a similar crystallisation, and cassava showing the least tendency for crystallisation, on freeze-thaw treatment.

7.6 Conclusions

The *Xanthosoma* starch gel exhibited a relatively stronger gel than cassava, *Alocasia*, and *Colocasia* starch gels, which exhibited similar gel strength. The *Xanthosoma* starch has extremely high tendency to undergo crystallisation and syneresis during freeze-thaw treatment compared to cassava, *Alocasia*, and *Colocasia* starches. Measurement of the rheological complex modulus G* can be used as a method of evaluating the freeze-thaw stability of starch gels.

CHAPTER EIGHT
GENERAL DISCUSSION AND CONCLUSIONS

8.1 Introduction

This research project was a preliminary study on the functional properties of three taro starches (*Xanthosoma, Colocasia*, and *Alocasia* starches). The different areas under investigation were the extraction of starches from the fresh taro, the granular physical and molecular characteristics of the starches, the starch gelatinization properties, some properties of the starch gels, and the freeze-thaw storage properties of the gels. The taro starches were compared with a commercial cassava starch product from Thailand.

8.2 The Starch Extraction Process

Previously, starch had been extracted from *Colocasia* and *Xanthosoma* (Moorthy, 1991) but there had been no reports of extraction of starch from *Alocasia*. The extraction of starch from fresh taro was proven to be an area that needs further investigation. This study attempted to use a simple conventional starch settling method which would be suitable for use in Tonga. The method involved grinding of fresh taro into taro pulp, washing the starch off the pulp, and collecting the starch milk (starch-water mixture) in a settling tank, holding the starch milk to allow starch to settle, and drying of starch. This method was successfully employed only in extraction of starch from the taro *Xanthosoma*. It was found that this starch effectively settled, with virtually no difficulties, into a solid starch cake at the bottom of the settling tank. The starch cake was easily recovered, after discarding the supernatant, and air dried.

The extraction method, however, did not work for *Colocasia* and *Alocasia* starches. After washing the starch off the taro pulp, the starch did not settle to form a solid starch cake at the bottom of the tank. The starch was separated from the starch milk using a bowl centrifuge.

It was suggested that the difficulty encountered in starch settling and separation were probably due to the presence of mucilaginous material which seemed to be thickening the starch milk, and causing a hindering effect on starch settling. This difficulty was also reported by Moorthy, (1991), when extracting starch from *Colocasia*. Moorthy (1991) suggested an extraction method which used dilute ammonia to facilitate starch settling. Unfortunately, this method was reported to alter the functional properties of the extracted starch. A suitable method for starch extraction from either *Colocasia* or *Alocasia* should be able to remove or dissolve the mucilaginous material allowing free settling of starch granules without altering the functional properties. Development of such method should involve a clear understanding of the precise structure and chemical nature of the mucilaginous material.

Another area that was not considered in this work was the effect of the raphide crystals in the taro starch extraction. Literature had reported the presence of raphide crystals in the aroid plants including taro (Sunell and Healey, 1979; Smith, 1982; Tang and Sakai, 1983; Bradbury and Holloway, 1988). These crystals are calcium oxalates which might chemically have some effect on the starch settling process. They should have been removed in the starch washing, but this removal needs to be confirmed.

8.3 The Granule Physical Characteristics

The physical characteristics of the starch granules were effectively studied using light microscopy. The granule size and shape of both *Colocasia* and cassava starch were consistent with those reported by other workers (Balagopalan et al., 1988; Agboola et al., 1990, Moorthy, 1991). There was no report on the granule physical characteristics of *Alocasia* and *Xanthosoma* starches. A more precise granule size measurement and a more defined structure detail could be obtained by the use of electron microscopy and more up-to-date equipment.

All the taro starches were polygonal in shape, as opposed to that of cassava which was round or oval in shape. The granule shape of the taro starches was similar to

that of maize, rice and sweet potato starches which had been reported to be also polygonal in shape. The granule size of *Xanthosoma* was similar to that of cassava starch. The granule sizes of *Alocasia* and *Colocasia* starches were very small compared with that of the cassava starch, and smaller than the granule size of rice starch. These taro starches were shown to have the smallest granule size of all the industrial starches, a special property of *Colocasia* and *Alocasia* starches. Because of the small granule size these starches were considered to be highly digestible and suitable for baby foods and diets of people allergic to cereals and children sensitive to milk. Other than food uses, the small granule size of these starches makes them suitable for cosmetic formulations like face powder and in dusting preparations which use aerosol dispensing systems (Griffin and Wang, 1983).

8.4 The Starch Molecular Characteristics

It was assumed that the starches were composed of amylose and amylopectin only and it was decided to determined only amylose contents. This was carried out using Morrison and Laignelet (1983) method. The amylose contents of cassava (19.4%) and *Colocasia* (13.6%) were both consistent with literature values of 16-18% (Balagopalan et al., 1988) for cassava starch and 10.8-19.4% (Sugimoto et al., 1986, and Moorthy et al., 1993). There was no report on the amylose contents of both *Xanthosoma* and *Alocasia* starches. The amylose content of the *Xanthosoma* starch (27%) was found to be higher than that of other starches. The amylose content of *Alocasia* (12%) was similar to that of *Colocasia* (14%).

Although the use of Morrison and Laignelet (1983) method seemed to offer reliable results, it would have been more appropriate to employ a second method for comparison. The use of only one method in this study was based on unavailability of necessary equipment needed for more intensive analysis such as the use of HPLC method of Govindasamy et al., (1992). The validity of the results of amylose determination relies largely on whether the assumption holds that the starches consisted only of amylose or amylopectin. There might be a significant percentage of a third intermediate component present in the starches which would have

influenced the functional properties of the starches. A detailed analysis of the precise molecular structures of the starches would clarify some of the grey areas encountered in this study.

The amylose content of *Xanthosoma* was similar to the amylose contents of maize (26%), wheat (25%), grain sorghum (26%), and sago (27%) starches (Knight, 1969). The *Xanthosoma* starch gel was expected to exhibit similar properties to those starches, especially the exhibition of high viscosity and pronounced set-back of starch gel. The amylose contents of *Alocasia* and *Colocasia* on the other hand were similar to that of rice (17%), and sweet potato (18%) starches (Knight, 1969). The *Alocasia* and *Colocasia* starches therefore were expected to exhibit similar properties to those starches, particularly the high viscosity, low set-back of gels.

8.5 The Functional Properties of the Starches

In studying the functional properties, the starches were investigated for their gelatinization properties and the gel physical and storage properties.

8.5.1 The Gelatinization Properties

Several methods were employed in studying the gelatinization properties of the test starches. These included sensory evaluation, hot stage microscopy, Brabender Amylograph, and Differential Scanning Calorimetry (DSC). These methods provided similar results for the gelatinization temperatures of the starches. It was considered that the Brabender Amylograph and DSC methods were more suitable for studying the starch gelatinization. Although the Brabender Amylograph is often considered by many food scientists to be too empirical, it still provides valuable fundamental practical information about the functional properties of starches, particularly the viscosity changes of starch gels at different temperatures. Many industrial applications of starch gels are based on their viscosity properties, and the Brabender Amylograph remains an easy way of obtaining this information.

The DSC method on the other hand, also provides valuable information on starches, particularly the enthalpy of gelatinization. Studying the gelatinization of starches based on the onset temperature of gelatinization can be misleading. The use of DSC to measure the enthalpy of gelatinization, is an effective way of gathering information related to molecular structure and molecular orientation within the granules which directly determine the functional properties of the starches.

The Gelatinization Temperature

The gelatinization temperature for the test starches were (±2°C): cassava 69, *Alocasia* 70, *Xanthosoma* 75, and *Colocasia* 80. The gelatinization temperatures for both cassava and *Colocasia* starches were consistent with those reported in literature (58-70°C for cassava, Balagopalan et al., 1988; and 67-73°C for *Colocasia*, Moy et al., 1977). The gelatinization temperature for *Xanthosoma* was lower than the range of 81-87°C, reported by Moorthy (1991). Differences may be attributed to different cultivars used in the analysis. There was no report on the gelatinization temperature of *Alocasia* starch. The gelatinization temperature of *Alocasia* covered a relatively wider temperature range (63-79°C). This was a rather unique feature of this starch and needs further investigation. It was found that there was no relationship between the gelatinization temperatures and amylose content or granule sizes.

The enthalpy of Gelatinization

In the DSC study of the starch gelatinization of the starches, the relative magnitude of the enthalpy (ΔH) of gelatinization for 30% w/w starches were: *Alocasia* 3.11, *Colocasia* 3.28, cassava 3.44, and *Xanthosoma* 4.64 J/g. There were no reports on the DSC analysis of gelatinization of *Alocasia, Colocasia*, or *Xanthosoma* starches. White et al., (1989) reported a value of 12 J/g (3 Cal/g) for 50% w/w cassava starch slurry.

The enthalpy of gelatinization was directly related to the amylose contents of the starches. It was suggested that because of the high amylose content, ie. the high

proportion of linear molecules, of *Xanthosoma* starch, the intermolecular associative forces were relatively higher, and required higher energy (J/g) to 'melt' or gelatinize it. The enthalpy of gelatinization for cassava, *Colocasia*, and *Alocasia* were similar. The enthalpy of gelatinization did not appear to be related to granule sizes.

The Swelling Power

The swelling power of the starches were measured as the amount of water absorbed by a known weight of dry starch sample when starch-water suspensions were heated at 85°C for 30 minutes (Schoch, 1964). The relative magnitudes of the swelling power for the test starches were: *Xanthosoma* 15.36, *Colocasia* 16.25, *Alocasia* 17.20, , and cassava 23.26 (g H_2O/ g dry starch). There were no reports on the swelling power of the test starches determined using this method. For the taro starches, the swelling power was shown to be increasing with decreasing amylose contents. It was suggested that the lower the amylose, and therefore the higher the amylopectin and more amorphous regions within the starch granules, allow easier penetration of water molecules and hence higher swelling power (Leach et al. 1965). Balagopalan et al. (1988) reported that a comparison of waxy and non-waxy varieties of rice, sorghum, and corn starches, showed that the higher amylose content led to lower swelling power, probably because of the linear molecules reinforcing the internal granular network. The relatively higher swelling power of the cassava starch than the taro starches was suggested in this study to be a factor of granule size rather than molecular structure.

Although this method provided useful information on the relative swelling power of the test starches, a more commonly used method of obtaining the swelling power for starches is determining the swelling power at every 5°C interval over the entire pasting range of the starches (Balagopalan et al., 1988). Leach et al. (1965) found that each species of starch showed a characteristic swelling pattern. This method, however, was not attempted in this study, because of time constraints.

8.4.2 Properties of the Starch Gels

Various properties of the starch gels were investigated. These included gel clarity, gel strength, and storage properties.

The Gel Clarity

The gel clarity was qualitatively studied by sensory evaluation. The starches were ranked from highest to lowest clarity as cassava, *Xanthosoma*, *Colocasia* and then *Alocasia*. Paste clarity is related to light reflectance of the gel, which reflects the differences in optical homogeneity within the granules with respect to uniformity of hydration (Kite et al., 1963). They also reported that there was a linear correlation between light transmission and swelling power. The cassava starch gel was very clear which corresponded to high swelling power. The *Colocasia* and *Xanthosoma* starch gels similarly showed poorer but compatible clarity to that of cassava starch gel. The *Alocasia* starch gel exhibited a rather poor clarity but this was probably due to some other unidentified discolouration effect. The cassava starch would be preferred to taro starches in food applications which require good gel clarity eg. in fruit pie fillings.

The Gel Strength

The gel strength of the freshly prepared starch gels were investigated using two methods: Instron penetration test and Bohlin rheological measurement. The Instron penetration test was a measure of the maximum force (N) required for a cone-shaped device to penetrate through the starch gels. The rheological measurement test was a measure of shear complex modulus G* of the gels, using a Bohlin Rheometer while heating over a temperature range of 25 to 90°C.

The relative magnitude of the force required to penetrate 10% w/w starch gels were: cassava 0.25, *Colocasia* 0.28, *Alocasia* 0.33, and *Xanthosoma* 2.04 N. The relative magnitude of the shear complex modulus G* of the gels at 25°C were: cassava 20.8,

Colocasia 29.8, *Alocasia* 33.3, and *Xanthosoma* 61.5 Pa. There were no reports of the use of these methods for measuring gel strength of these starches.

Both of these tests showed the same order of gel strength. The cassava, *Alocasia* and *Colocasia* showed similar gel strengths. The *Xanthosoma* showed a much higher gel strength. The high gel strength of the *Xanthosoma* starch could be related to the high amylose content. As the starch gelatinized, the amylose molecules solubilised and diffused out of the starch granules to form the three-dimensional gel network. Because of the high number of amylose molecules that form the gel network, the gel was stiffer (Miles et al. (b) 1985), showing higher penetrating force and complex G* modulus. The relatively low strength of the cassava starch which had relatively high amylose content, could probably be attributed to some other unidentified mechanism. Because of the high strength of *Xanthosoma* it could be used in food formulations like instant soup where only addition of water and heating are required in preparation for consumption. Its high gel strength could allow the use of a little amount to provide the required texture of the product.

The Gel Storage Stability

The gel storage stability of the starch gels was evaluated using two methods: measurement of enthalpy of crystallisation after storage using DSC and measurement of the syneresis after storage. The enthalpy of crystallisation was expressed as percentages of gelatinization. This was carried out by scanning the starch suspensions to get the enthalpy of gelatinization, and the samples were stored and then scanned again to get the enthalpy of crystallisation. Syneresis was a direct measure of the weight (expressed as percentage) of water separated from the gels after storage. The gels were centrifuged after storage and the separated water was weighed. Starch gels were stored at 5 and 22°C for 10 days before they were evaluated for crystallisation. The relative magnitudes of crystallisation for 30% w/w starch gels stored at 5°C were: *Colocasia* 34, cassava 41, *Alocasia* 45, and

Xanthosoma 54%. The relative magnitudes of syneresis for 5% w/w starch gels after storage at 5°C for 8 days were: cassava 0.5, *Alocasia* 0.5, *Colocasia* 4.1, and *Xanthosoma* 45.3%.

Both of these methods showed that the cassava, *Colocasia*, and *Alocasia* starch gels had similar stability and were more stable in storage at 5°C than the *Xanthosoma* starch gel.

The gel stability of cassava starch has been reported to be much higher compared to cereal starches and hence is preferred for many food products, especially when the food has to be stored for a longer time (Balagopalan et al., 1988). Comparing cassava with taro starches, the gel stability of the *Colocasia* and *Alocasia* starches were similar to that of the cassava starch. The *Xanthosoma* starch can not be used to replace cassava because of poor storage stability.

The Freeze-Thaw Stability of the Starch Gels

The freeze-thaw stability of the gels was evaluated using Bohlin rheological measurement, Instron penetration and tensile strength tests, syneresis measurement, and crystallisation measurement. The tensile strength, was carried out by measuring the force required to break gel rings. The other measurements were carried out in the same way as previously described.

The complex shear modulus G* of 5% gels, subjected to repeated freeze-thaw (FT) cycles, were measured. The relative magnitudes of G* of the gels at 26°C after 2 FT cycles were: cassava 493, *Alocasia* 507, *Colocasia* 527 and *Xanthosoma* 1980 Pa. The magnitude of the G* was considered to correspond to the degree to which crystallisation had occurred during the freeze-thaw treatment (Miles et al. (a), 1985). The results showed that the *Xanthosoma* starch gel was extremely susceptible to crystallisation during freeze-thaw treatment compared with cassava, *Colocasia*, and *Alocasia* starch gels, which exhibited similar G* modulus at 26°C.

The attempt to measure the tensile strength of the gel rings was not successful. The results of replicate samples exhibited extremely high errors and were not used for drawing conclusions about the starch gels. The high errors were probably attributed to the size of the rings being too large.

The Instron penetration test of 10% w/w starch gels showed relative penetrating forces of after 4 FT cycles: *Alocasia* 4.1, *Colocasia* 4.3, cassava 6.0, and *Xanthosoma* 14.7 N. The syneresis test showed a relative magnitudes of syneresis for 5% w/w starch gels after 1 FT cycle of: cassava 8, *Colocasia* 29, *Alocasia* 33 and *Xanthosoma* 42 %. The relative crystallisation of 7% w/w starch gels after 4 FT cycles were cassava 14, *Colocasia* 30, *Alocasia* 42, and *Xanthosoma* 50%.

These results showed that the *Xanthosoma* starch gel was extremely susceptible to crystallisation during freeze-thaw treatment. The cassava showed the highest gel stability on freeze-thaw treatment, as indicated by lowest syneresis, and crystallisation. The *Colocasia* and *Alocasia* starch gels showed similar freeze-thaw stability. Compared with cassava starch gel, they exhibited poorer freeze-thaw stability due to higher syneresis and crystallisation.

These results proved cassava starch to be a better starch to use to use in food applications where repeated freeze-thaw treatment is required. The *Alocasia* and *Colocasia* gels were comparable with the cassava starch gel. Because of low amylose contents of these starches, modification by derivatization may enhance their freeze-thaw stability. The *Xanthosoma* starch cannot be used for freeze-thaw products.

8.6 General Conclusions

This study showed that the *Xanthosoma* starch was very different to *Colocasia, Alocasia* and cassava starches in most functional properties. It was comparable with cassava starch in gel strength and paste clarity; but the storage stability of the gel was very poor. It produced an extremely viscous paste which could make it useful in food products which require high viscosity but need no further storage. The *Colocasia* and *Alocasia* starches had similar properties to cassava starch in terms of gel strength but had poorer gel storage properties and paste clarity. They could be used to replace cassava in applications where paste clarity is not a major consideration. The small size granules of these starches provides higher digestibility which makes them suitable for baby food formulations.

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Appendix

Appendix 1: Chemical Composition of Taro

Table A1: Composition of taro *Colocasia* cultivars from Western Samoa (Bradbury and Holloway, 1988)

Sample designation		*Manua*	*Pa'epa'e*	*Niue*	*Fa'ele'ele*	*Mean*[b]	*SD*
Moisture %	a	72.9	72.2	72.7	67.9	71.4	2.4
		(5.8)	(5.0)	(1.5)	(4.0)		
Energy (kg/100 g)							
E_a		435	430	390	461	429	30
E_b		432	444	435	519	458	41
Protein %	b	1.01	1.15	0.82	0.56	0.89	0.26
		(0.26)	(0.51)	(0.29)	(0.07)		
Starch %	e	23.8	23.8	21.8	26.0	23.9	1.7
		(5.8)	(5.0)	(1.8)	(3.7)		
Sugar %	f	0.66	0.29	0.21	0.44	0.40	0.20
		(0.35)	(0.24)	(0.13)	(0.03)		
Dietary fibre %	g	1.28	1.28	1.25	1.11	1.23	0.08
		(0.22)	(0.30)	(0.09)	(0.06)		
Fat %	c	0.10	0.06	0.05	0.06	0.07	0.02
		(0.03)	(0.02)	(0.03)	(0.03)		
Ash %	d	0.57	0.72	0.84	0.85	0.75	0.13
		(0.08)	(0.17)	(0.14)	(0.13)		
Calcium (mg/100 g)		18.6	33.4	18.0	33.2	25.8	8.7
		(5.0)	(8.9)	(3.6)	(1.1)		
Iron (mg/100 g)		0.29	0.38	0.41	0.44	0.38	0.06
		(0.07)	(0.11)	(0.05)	(0.06)		
Trypsin Inhibitor (TIU/g)		zero	26.4	2.5	6.3	8.8	2.0

[a] Samples obtained April 1984. Cultivar Niue accounts for about 75% of total production and Manua and Pa'epa'e are also very popular. Five corms of each of the first three cultivars were analysed and the results averaged, and two corms of the last cultivar.

[b] Sum of a + b + c + d + e + f + g = 98.6.

Table A2: Taro (*X. sagittifolium*) composition of edible corms and leaves from different literature sources

(Bradbury and Holloway, 1988)

	Corms						Edible leaves
	Present work						
	Table A.25	Table A.26	Mean	Parkinson (1984a)	Standal (1982)	Onwueme (1978)	Chowdhury and Hussain (1979)
Number of samples and country	27 samples 3 cv (from Tonga)	10 samples 2 cv (from PNG)		Food Comp. Table, East Asia, FAO 1972		Range of values	2 samples
Moisture %	68.1	66.0	67.1	75.4	65	70–77	83.9
Energy (kJ/100 g)	496	545	521	393	560	—	—
Protein %	1.44	1.66	1.55	2.2	2.0	1.3–3.7	3.5
Starch %	25.7	29.4	27.6	—	—	—	—
Sugar %	0.57	0.27	0.42	—	—	—	—
Carbohydrate % (diff.)	—	—	—	21.0 incl. crude fibre	31.0	17–26	—
Dietary fibre %	1.15	0.82	0.99	—	—	—	—
Crude fibre %	—	—	—	—	—	0.6–1.9	3.02
Fat %	0.12	0.10	0.11	—	0.3	0.2–0.4	1.66
Ash %	1.12	0.96	1.04	—	—	0.6–1.3	1.90
Total oxalate[a] (mg/100 g)	60	—	—	—	—	—	680
Calcium oxalate (mg/100 g)	23	—	—	—	—	—	—
Minerals (mg/100 g)							
Ca	5.9	11.1	8.5	34	20	—	283
P	53	—	53	62	—	—	61
Mg	27	—	27	—	—	—	51
Na	6.6	—	6.6	—	—	—	8.7
K	530	—	530	448	—	—	—
S	7.9	—	7.9	—	—	—	—
Fe	0.47	0.33	0.40	1.2	1.0	—	5.9
Cu	0.19	—	0.19	—	—	—	—
Zn	0.52	—	0.52	—	—	—	—
Mn	0.17	—	0.17	—	—	—	—
Al	0.53	—	0.53	—	—	—	—
B	0.09	—	0.09	—	—	—	—
Vitamins (mg/100 g)							
Vitamin A (ret. + β-car./6)	0.005	—	0.005	tr	0	0.33	4.5
Thiamin	0.024	—	0.024	0.12	1.1	0.06	—
Riboflavin	0.032	—	0.032	0.04	0.03	0.2	—
Nicotinic acid	0.80	—	0.80	1.0	0.5	1	—
Pot. Nic. acid = Trp/60	0.33	—	0.33	—	—	—	—
Vitamin C	13.6	—	13.6	8	10	96	65
Limiting amino acids and score							
First	Lysine 57	—	Lys 57	—	—	—	—
Second	Leucine 81	—	Leu 81	—	—	—	—
Trypsin inhibitor (TIU/g)	0.3	—	0.3	—	—	—	—
Edible matter, prop. of wt. purchased	—	—	—		0.77–0.86	—	—

[a]Results for other organic acids and free calcium given in Table A.25.

Table A3: Giant taro (*A. macrorrhiza*) composition of corms and leaves from different literature sources

	Corms				Edible leaves
	Present work Table 3.7	*South Pacific Comm. (1983)*	*Sakai (1983)*	*Parkinson (1984a,b)*	*(Sakai 1983)*
Number of samples and country	*37 samples from W. Samoa and Tonga*	*Source is Murai et al. (1958) Hawaii*	*Various sources*		*Bangladesh*
Moisture %	70.3	81.3	63–87	84	—
Energy (kJ/100 g)	449	290	290–600	255	—
Protein %	2.15	0.6	0.6–3.3	0.6	0.3–4.3
Starch %	21.5	—	—	—	—
Sugar %	0.96	—	0.5	—	—
Carbohydrate % (diff.)	—	16.9	3–20	14.8	4–6
Dietary fibre %	1.85	—	—	—	—
Crude fibre %	—	—	1–3	—	1–2.7
Fat %	0.10	0.1	0.02–0.9	—	0.1–0.9
Ash %	0.92	—	0.8–1.4	—	0.8–1.4
Total oxalate (mg/100 g)	38	—	150	—	—
Minerals (mg/100 g)					
Ca	38	152	46–160	30	57–235
P	44	45	45–72	50	25–99
Mg	52	—	—	—	—
Na	30	—	—	—	—
K	267	—	—	—	—
S	11.9	—	—	—	—
Fe	0.83	0.5	0.5–1.0	1.0	0.6–3.8
Cu	0.07	—	—	—	—
Zn	1.51	—	—	—	—
Mn	0.62	—	—	—	—
Al	0.36	—	—	—	—
B	0.10	—	—	—	—
Vitamins (mg/100 g)					
Vitamin A (ret. + β-car./6)	0	—	tr	0	0.15–2.2
Thiamin	0.021	0.10	0.01–0.1	0.05	0.01–0.09
Riboflavin	0.018	0.02	0.01–0.03	—	0.01–0.34
Nicotinic acid	0.48	0.4	0.4	—	—
Pot. Nic. acid = Trp/60	0.46	—	—	—	—
Vitamin C	17.0	tr	0–7	5	5
Limiting amino acids and score					
First	Lysine 64	—	—	—	—
Second	His 91, Ileu 93	—	—	—	—
Trypsin inhibitor (TIU/g)	269	—	—	—	—
Chymotrypsin inhibitor (CIU/g)	57	—	—	—	—
Edible matter, prop. of wt. purchased	—	—	0.82	—	—

Appendix 2: Selection of Taro Cultivars for the Study

Introduction

The selection of taro cultivars for the study was based on pre-determined factors. These factors were: starch contents, size of the starchy edible parts (corms or cormels), time to maturity, commonly grown for commercial purposes in Tonga.

For each of the three most commonly grown taro genera in Tonga, *Colocasia, Alocasia*, and *Xanthosoma,* the three most commonly grown cultivars were scored for each of the scoring factors. Each factor was given an arbitrary scale of 1 to 9 points. The scores for each cultivars were added to give a total score. The cultivars with the highest scores were selected for the study. The scores for starch content were based on the results of Bradbury and Holloway (1988). The other factors were scored based on background experiences of the writer.

The arbitrary point scales for the selecting factors were as follows.

Factors

A	Starch content	lowest	highest
		|----------|	
		1 9	
B	Size of starchy	smallest	largest
	edible part	|----------|	
		1 9	
C	Time to maturity	longest	shortest
		|----------|	
		1 9	
D	Grown for commercial	less common	most common
	purpose	|----------|	
		1 9	

Results

Tables A4, A5, and A6 summarise the results.

Table A4: ***Colocasia*** **cultivars**

	Cultivars		
	Lau'ila	Kula	'Uli
A	6	5	6
B	7	8	5
C	8	4	4
D	8	6	3
Total	29	23	18

Table A5: ***Alocasia macrorrhiza*** **cultivars**

	Cultivars		
	Hina	Tuu	Fohenga
A	6	4	9
B	8	6	7
C	8	7	7
D	8	4	8
Total	30	21	31

Table A6: ***Xanthosoma sagittifolium*** **cultivars**

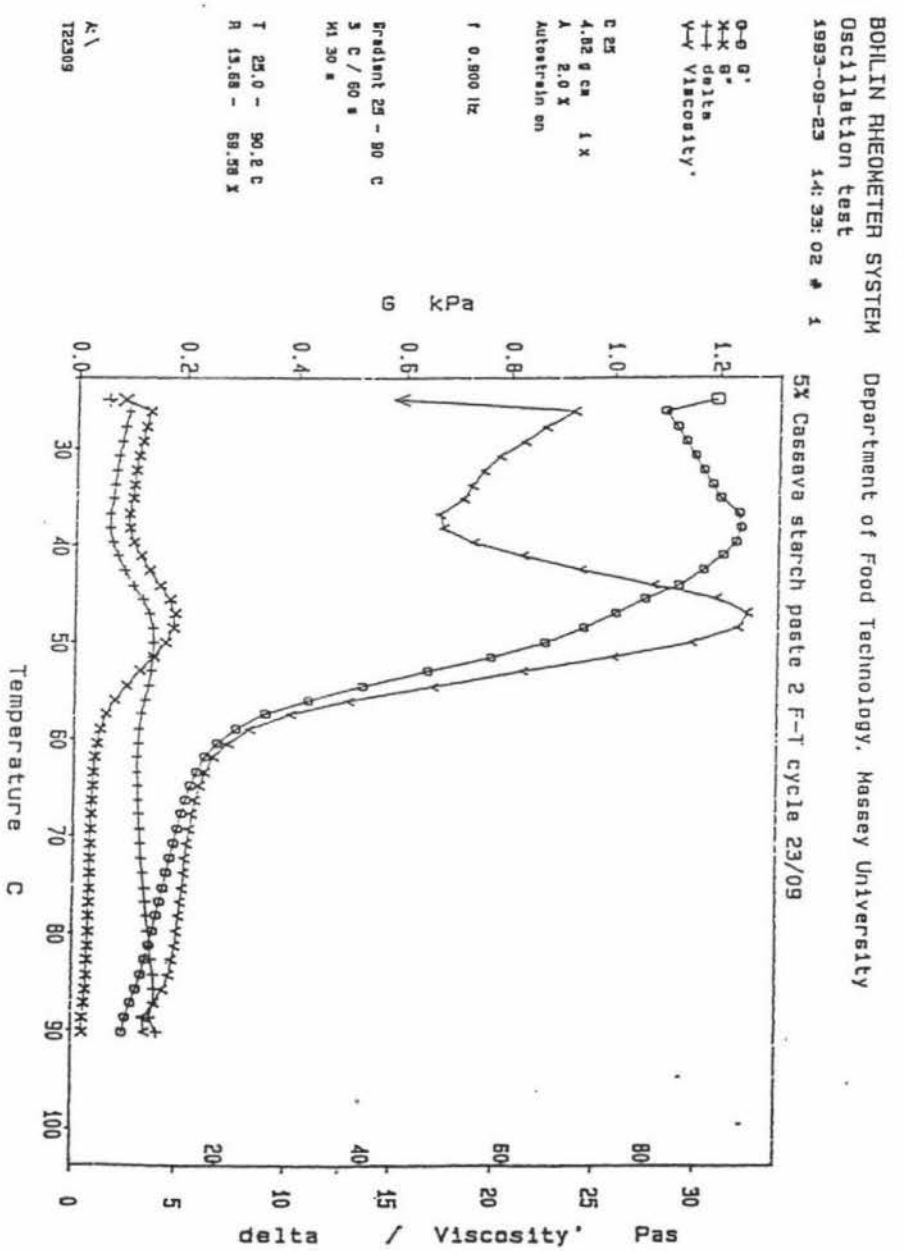
	Cultivars		
	Futuna	Mahele'uli	Tea
A	4	9	7
B	7	8	6
C	8	8	7
D	8	8	8
Total	27	31	28

Conclusion

From the basis of these tables the selected cultivars for the study were: *Colocasia esculenta* var *'Lau'ila'*, *Alocasia macrorrhiza* var *'Fohenga'*, and Xanthosoma sagittifolium var *'Mahele'uli'*.

Appendix 3A: A sample of recorded data from a Bohlin rheometer measurement (Oscillation mode)

```
epartment of Food Technology, Massey University          BOHLIN RHEOMETER SYSTEM
                                                         Oscillation test
% Alocas starch paste time effect 15/11                  1993-11-15  16:40:02
   1
easuring system: C 25
orque element: 42.9 g cm                    Sensitivity: 1 x  Amplitude: 5 %
emperature:   Gradient 25 - 90 xC,  3 xC / 60 s
easurement interval: 30 s                   Time at end temperature 0 s
hermal equilibrium time: 30 s
ootstrain off
:\
ile name: A931511
```

Time s	Temp xC	Freq Hz	Phase	Viscosity Pas	G* Pa	G' Pa	G" Pa	Range %	Ampl %	Corr	Strain
0	25.0	.9	8.5	7.20E+1	2.76E+3	2.73E+3	4.09E+2	17.79	5.0	0.36	.00667
30	26.2	.9	8.4	7.12E+1	2.77E+3	2.74E+3	4.03E+2	17.83	5.0	0.36	.00667
60	27.9	.9	8.1	6.97E+1	2.79E+3	2.76E+3	3.94E+2	17.91	5.0	0.36	.00666
90	29.3	.9	8.0	6.85E+1	2.80E+3	2.77E+3	3.88E+2	17.97	5.0	0.36	.00665
120	30.8	.9	7.8	6.76E+1	2.82E+3	2.79E+3	3.82E+2	18.05	5.0	0.36	.00663
150	32.3	.9	7.6	6.61E+1	2.84E+3	2.81E+3	3.74E+2	18.13	5.0	0.36	.00662
180	33.8	.9	7.5	6.58E+1	2.85E+3	2.83E+3	3.72E+2	18.19	5.0	0.36	.00661
210	35.2	.9	7.4	6.53E+1	2.87E+3	2.85E+3	3.69E+2	18.27	5.0	0.37	.00659
240	36.8	.9	7.2	6.43E+1	2.89E+3	2.87E+3	3.64E+2	18.35	5.0	0.37	.00658
270	38.2	.9	7.1	6.36E+1	2.90E+3	2.88E+3	3.59E+2	18.41	5.1	0.37	.00657
300	39.6	.9	7.0	6.32E+1	2.91E+3	2.89E+3	3.57E+2	18.46	5.1	0.37	.00656
330	41.2	.9	7.0	6.28E+1	2.93E+3	2.91E+3	3.55E+2	18.52	5.1	0.37	.00655
360	42.7	.9	6.9	6.26E+1	2.93E+3	2.91E+3	3.54E+2	18.53	5.1	0.37	.00654
390	44.2	.9	6.9	6.20E+1	2.93E+3	2.91E+3	3.50E+2	18.53	5.1	0.37	.00654
420	45.7	.9	6.8	6.15E+1	2.92E+3	2.90E+3	3.48E+2	18.47	5.1	0.37	.00655
450	47.1	.9	6.9	6.10E+1	2.89E+3	2.87E+3	3.45E+2	18.35	5.1	0.37	.00658
480	48.7	.9	6.9	6.04E+1	2.84E+3	2.81E+3	3.42E+2	18.13	5.0	0.36	.00662
510	50.2	.9	7.0	5.92E+1	2.76E+3	2.74E+3	3.35E+2	17.82	5.0	0.36	.00668
540	51.6	.9	7.0	5.75E+1	2.68E+3	2.66E+3	3.25E+2	17.50	5.0	0.35	.00675
570	53.1	.9	6.9	5.48E+1	2.59E+3	2.57E+3	3.11E+2	17.10	5.0	0.34	.00683
600	54.6	.9	6.8	5.20E+1	2.50E+3	2.48E+3	2.94E+2	16.68	5.0	0.33	.00691
630	56.1	.9	6.6	4.92E+1	2.41E+3	2.39E+3	2.78E+2	16.27	5.0	0.33	.00700
660	57.6	.9	6.4	4.69E+1	2.32E+3	2.30E+3	2.60E+2	15.84	5.0	0.32	.00708
690	59.1	.9	6.2	4.30E+1	2.24E+3	2.22E+3	2.43E+2	15.46	5.0	0.31	.00716
720	60.6	.9	6.0	4.04E+1	2.17E+3	2.16E+3	2.28E+2	15.13	5.0	0.30	.00722
750	62.1	.9	5.9	3.83E+1	2.11E+3	2.10E+3	2.17E+2	14.82	5.0	0.30	.00728
780	63.5	.9	5.8	3.64E+1	2.06E+3	2.05E+3	2.06E+2	14.56	5.0	0.29	.00733
810	65.0	.9	5.8	3.60E+1	2.02E+3	2.01E+3	2.04E+2	14.37	5.0	0.29	.00737
840	66.4	.9	5.7	3.48E+1	1.98E+3	1.97E+3	1.97E+2	14.18	5.0	0.29	.00740
870	67.9	.9	5.8	3.49E+1	1.95E+3	1.94E+3	1.97E+2	14.02	5.0	0.28	.00744
900	69.5	.9	6.1	3.60E+1	1.92E+3	1.91E+3	2.04E+2	13.85	5.0	0.28	.00747
930	71.0	.9	8.0	4.54E+1	1.84E+3	1.82E+3	2.57E+2	13.41	5.0	0.27	.00757
960	72.4	.9	12.1	5.72E+1	1.55E+3	1.51E+3	3.23E+2	11.63	5.0	0.23	.00792
990	73.9	.9	13.4	5.87E+1	1.43E+3	1.40E+3	3.32E+2	11.17	5.0	0.22	.00806
1020	75.5	.9	14.9	6.51E+1	1.44E+3	1.39E+3	3.68E+2	11.18	5.0	0.22	.00807
1050	76.9	.9	15.7	7.03E+1	1.47E+3	1.42E+3	3.96E+2	11.40	5.0	0.22	.00803
1080	78.4	.9	15.1	7.04E+1	1.53E+3	1.47E+3	3.98E+2	11.73	5.0	0.23	.00795
1110	79.9	.9	11.9	6.01E+1	1.65E+3	1.61E+3	3.40E+2	12.40	5.0	0.25	.00779
1140	81.4	.9	7.9	4.15E+1	1.71E+3	1.70E+3	2.34E+2	12.73	5.0	0.26	.00770
1170	82.9	.9	12.4	5.54E+1	1.46E+3	1.42E+3	3.14E+2	11.27	5.0	0.22	.00802
1200	84.4	.9	21.6	6.98E+1	1.07E+3	9.96E+2	3.95E+2	8.68	5.0	0.17	.00859
1230	85.9	.9	38.7	8.79E+1	7.95E+2	6.21E+2	4.97E+2	7.02	5.0	0.11	.00915
1260	87.2	.9	47.2	8.86E+1	5.28E+2	3.59E+2	3.88E+2	4.90	5.0	0.07	.00961
1290	88.7	.9	34.6	1.04E+2	1.03E+3	8.50E+2	5.87E+2	8.75	5.0	0.15	.00877
1320	90.2	.9	10.9	5.46E+1	1.63E+3	1.60E+3	3.09E+2	12.26	5.0	0.24	.00780

Appendix 3B: A sample of typical plot from the Bohlin rheometer measurement (Oscillation mode)