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Food Chemistry 91 (2005) 203–211

Food Chemistry

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# Pasting, swelling and solubility properties of UV initiated starch-graft-poly(AA)

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Received 3 May 2002; received in revised form 14 August 2003; accepted 14 August 2003

**Abstract**

UV-initiated graft copolymerization of sago starch with acrylic acid (AA) at low level (2.5%, 5%, 7.5% and 10% w/w) was investigated. The UV curing technique and procedure was found to successfully produce starch-graft-poly(acrylic acid) [S-g-poly-(AA)]. The carboxyl group content was found to increase with increasing % of monomer. Rapid visco-analyzer (RVA) pasting profile, swelling and solubility of the samples were studied. UV irradiation of sago starch (control) results in high pasting temperature, high peak viscosity and high setback, besides retarding swelling and solubility as compared to the native untreated starch ($p < 0.05$). Pasting temperature was decreased after grafting as compared to the control. S-g-poly(AA) showed higher peak viscosity, peak time and setback than native untreated starch ($p < 0.05$). Breakdown was retarded at 2.5% S-g-poly(AA) but increased at 10%. S-g-poly(AA) exhibited lower swelling power and solubility than the native sample ($p < 0.05$).

## 1. Introduction

Starch had been a subject of academic as well as of industrial interest for the past few decades. Besides its low cost and availability, the biodegradability has gained even more importance in this environmentally concerned era. Graft polymerization of monomers is one of the universal, effective and accessible methods of chemical modification of high molecular weight compounds, and natural polymers in particular (Lutfor et al., 2000). Grafting can be carried out in such a way that the properties of the side chains can be added to those of the substrate polymers without greatly changing the latter. Chemical modification of starch via vinyl graft copolymerization constitutes a powerful means of improving starch properties, thereby enlarging the range of its utilization (Mostafa, 1995).

Graft copolymerization of starch with acrylic acid has found extensive commercial applications, especially as hydrogels for personal care products, in construction of buildings, food packages, medical applications and agricultural applications (Athawale & Lele, 2001). Starch graft copolymers can be achieved, primarily, by free radical-initiated processes. As with other free radical polymerizations, starch-graft-poly(acrylic acid) [S-g-poly(AA)] copolymer can be prepared through either chemically initiated or radiation-induced process. Extensive work has been reported for the chemical copolymerization of vinyl monomers to starch (Athawale & Lele, 1998; Bayazeed, Elzairy, & Hebeish, 1989; El-Rafie, Zahran, El Tahlawy, & Hebeish, 1995; Gao, Tian, Yu, & Duan, 1994; Mostafa, 1995; Rahman et al., 2000) but less is known about the corresponding radiation-induced process. Emphasis has been placed only on high energy ionization radiation, especially $\gamma$-rays (Burr, Fanta, Doane, & Russell, 1976; Fanta, Burr, & Doane, 1979; Kiatkamjornwong & Meechai, 1997; Kiatkamjornwong, Chomsaksakul, & Sonsuk, 2000). Electron beam and ultraviolet (UV) irradiation has also been reported to initiate grafting on starch (Fanta & Doane, 1986).

This paper describes the grafting of sago starch with acrylic acid (AA) using a UV irradiation technique. UV-radiation curing has become a well-accepted environmentally friendly technology which, because of its

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0308-8146/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/j.foodchem.2003.08.032

distinct advantages, has found many industrial applications, particularly as a fast curing method for protective coatings, printing inks and adhesives (Masson, Decker, Jaworek, & Schwalm, 2000). Wuertz, Bismarck, Springer, and Königer (1999) also mentioned the following advantages of UV-induced polymerization over other crosslinking techniques, i.e., fast curing rate at room temperature, spatial and temporal control of the polymerization, the ability to place the gel in vivo without surgical intervention and minimal heat production.

In free radical-initiated graft copolymerizations involving starch, a free radical produced on starch reacts with a monomer to form a grafted copolymer (Kiatkamjornwong & Meechai, 1997). A photoinitiator is required in UV-radiation curing to absorb a photon from a UV light source and then to form the initiator radical. The initiator radical will then react with starch to create a free radical for grafting. The main desirable factor for the choice of photografting by UV in this work was the rapid grafting rate as compared to the conventional chemical process. Our objective was to produce sago starch-grafted poly(acrylic acid) by UV irradiation and to characterize the pasting, swelling and solubility properties of the grafted starch at a low level of modification (2.5%, 5%, 7.5% and 10% of acrylic acid, w/w of starch). The effect of UV irradiation on sago starch under the grafting conditions is studied accordingly.

## 2. Materials and methods

### 2.1. Materials

Sago starch (*Metroxylon* sagu) was purchased from Nitsei Sago Industries Sdn. Bhd., Butterwotrh, Penang. 2-Hydroxy-4′-hydroxyethody-2-methylpropiophenone (Irgacure, 2959) was supplied by Ciba Specialty Chemicals, Singapore. Acrylic acid (Fluka, >99% purity) was used as received without further purification. Other chemicals were of analytical reagent grade. Glass-distilled water was used throughout.

### 2.2. Preparation of S-g-poly(AA)

About 0.4 g (2% w/w, of starch) of photoinitiator (Irgacure, 2595) was added to 20 ml of distilled water. The mixture was heated (90–95 °C) to dissolve the photoinitiator and then cooled before adding to 20 g of sago starch and the required amount of acrylic acid (2.5%, 5%, 7.5% and 10% w/w). Starch was dispersed in the solution by vigorous stirring, using a spatula, and poured immediately onto a 18 cm × 8 cm × 0.1 cm glass plate. The solution was then spread evenly on the glass plate. UV curing was performed by passing the glass plate under a M200U2 UV lamp ($\lambda$ = 180–450 nm, 200 W/in.) at a speed of 5 m/min.

After curing, 200 g of modified starch (approximate yield of 10 batches) was scraped off and collected in a 2 l beaker and washed five times with 500 ml of hot boiling ethanol (85%) to remove the homopolymer (Bayazeed et al., 1989). Each washing was carried out for 15 min while the starch slurry was continuously stirred by a magnetic stirrer. Lastly, 500 ml of 85% ethanol was added to the modified starch and centrifuged to separate the solid. S-g-AA was dried at 70 °C overnight in a hot air oven. The starch sample was then ground to 0.2 μm using a hammer mill (Glen Greston, England, Type: DCFH 48). Control sago starch was prepared using the same procedure but without the monomer, acrylic acid.

### 2.3. Infrared spectral analysis

The infrared spectra of native untreated, control and grafted starch were obtained on KBr pellets of the samples, using a Perkin Elmer System 2000 Spectrophotometer in the frequency range of 4000–400 $\text{cm}^{-1}$.

### 2.4. Determination of carboxyl group content

Determination of % grafting was based on hot paste titration of the grafted starch for the carboxyl group content. The carboxyl group content was determined according to the procedure of ISO 11214 by International Starch Institute (ISI 10, 1998). Mean values of duplicate determinations were obtained for each sample.

### 2.5. Moisture determination

The procedure of James (1995) with minor modification was employed. Approximately 5 g of sample was weighed into a pre-dried and cooled aluminium dish and dried at 105 °C in a hot air oven for 4 h. The sample was then cooled in a desiccator, weighed and re-dried for another 1 h in the oven. The drying–cooling–weighing cycle was repeated to constant weight. The loss of weight was equated to the moisture content of the sample. Mean values of three determinations were obtained.

### 2.6. Rapid visco-analyzer (RVA) profile analysis

A RVA (Newport Scientific Pvt. Ltd., Narrabeen, Australia) was employed to determine the pasting profile of the sample. About 2.5 g of starch sample (corrected to 14% moisture basis) and a measured amount (25 ml) of distilled water were combined and stirred in the aluminium RVA sample canister. A programmed heating and cooling cycle was used; the temperature profile was taken from the ICC Standard Method No. 162, profile No. 1. The paddle speed was set at 960 rpm for the first

10 s to evenly disperse the starch slurry and reduced to 160 rpm throughout the entire experiment. The units of viscosity were expressed as RVU. Four determinations were averaged for each sample.

### 2.7. Swelling power and solubility

Swelling power and solubility of starch samples were determined by the procedure described by Schoch (1964) with minor modification. Approximately 2 g of sample was used in each determination. To determine the soluble starch, 30 ml aliquot of the supernatant was dried overnight in an air oven at 130 °C. Triplicate experiments were carried out for each sample.

### 2.8. Experimental design and statistical analysis

Statistical analyses were performed with the SPSS 10.1 Window package. One way ANOVA (Analysis of variance) and Tukey's multiple comparison test were performed and significance was defined at $p < 0.05$.

## 3. Results and discussion

### 3.1. Evidence of grafting

#### 3.1.1. Infrared spectral analysis

The IR spectra of native untreated, control (UV irradiated) and grafted starch (Figs. 1 and 2) showed a broad absorption band characteristic of the glucosidic ring of starch, from 3450 to 3200 cm$^{-1}$. Other bands, such as those at about 2930 cm$^{-1}$ (C–H stretching), 1650 cm$^{-1}$ (absorbed water), 1423 cm$^{-1}$ ($CH_2$ bending) and peaks around 1150–1040 cm$^{-1}$ (C–O stretching) due to alcoholic hydroxyl groups, can also be seen. From Fig. 2, spectra of S-g-AA showed a new band at 1730 cm$^{-1}$ (acidic C=O stretching) suggesting the existence of grafting. Only a trailing shoulder can be detected when 2.5% of AA was used in the grafting. When the amount of the AA was increased, the carbonyl band became more pronounced (fixed amount and ratio of KBr and sample was employed while scanning so as a relative comparison could be done). This indicates that the degree of grafting increases with monomer content. The spectrum of control was similar to the native untreated starch (Fig. 1), which indicates that the granular structure of UV-irradiated starch basically remained intact.

#### 3.1.2. Carboxyl group content

According to the method of Trimnell and Stout (1980), the amounts of grafted poly(acrylic acid) in the graft copolymer were determined by carboxyl content, either indirectly by treatment with excess base, followed by back titration with hydrochloric acid, or direct titration to the phenolphthalein endpoint. In this work, direct titration on hot starch paste was employed.

Table 1 shows that % of carboxyl group (–COOH) increased with increasing of monomer (AA) % in the grafting process. This is a very general trend that has

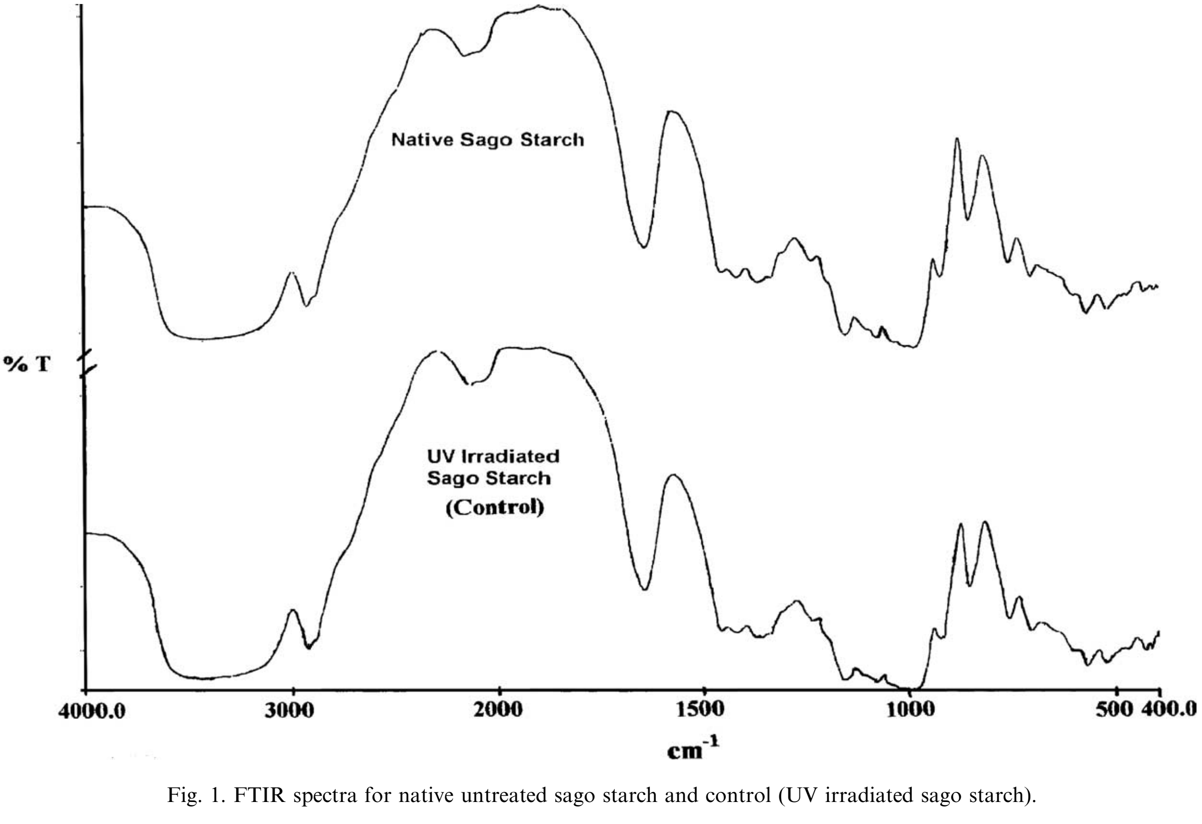

Fig. 1. FTIR spectra for native untreated sago starch and control (UV irradiated sago starch).

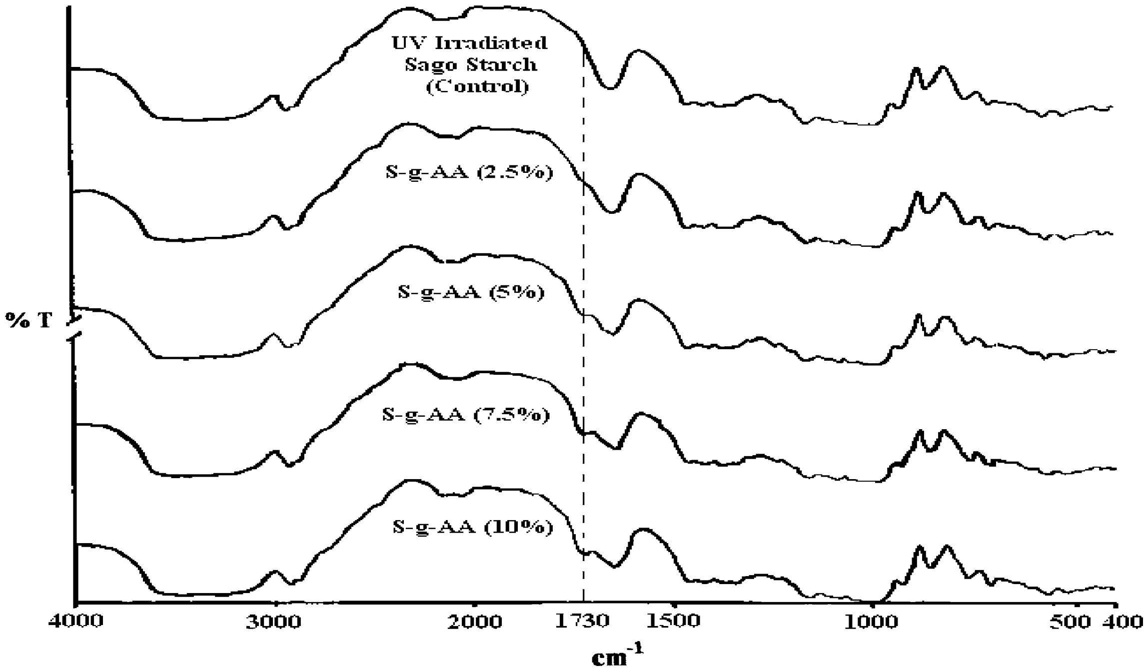

Fig. 2. FTIR spectro for control (UV-irradiated starch) and S-g-AA copolymers.

Table 1
Carboxyl group content for UV-initiated S-g-poly(AA) at different percentages of acrylic acid (AA) monomer

| S-g-poly(AA) | % COOH[a] |
|---|---|
| 2.5% AA | 0.31 |
| 5% AA | 0.61 |
| 7.5% AA | 0.77 |
| 10% AA | 0.98 |

% AA indicates % of acrylic acid used in the graft copolymerization.

[a] COOH is based on dry basis. The results are averages of duplicate.

Table 2
Moisture content (%) of native untreated sago starch, control and S-g-AA copolymers

| Sample | Moisture content (%)[a] |
|---|---|
| Native untreated sago starch | 14.56 |
| Control (UV-irradiated starch) | 5.61 |
| 2.5% AA | 6.53 |
| 5% AA | 4.57 |
| 7.5% AA | 4.02 |
| 10% AA | 2.86 |

% AA indicates % of acrylic acid used in the graft copolymerization.

[a] Results are averages of triplicates.

been found in other grafting systems. During the grafting process, monomer continuously diffuses into the polymeric matrix. The ability of starch macroradicals to capture AA would depend on the availability of AA molecules in their vicinity. The increase in AA % will therefore lead to an increase in graft content. Increase also increases moisture content (Table 2).

### 3.2. Pasting properties

### 3.2.1. General

The viscosity changes observed upon heating and cooling of starches in excess water will provide a characteristic pasting curve.

### 3.2.2. Pasting temperature, peak time and peak viscosity

As shown in Table 3, control sample pastes at higher temperature than native untreated and grafted starch ($p < 0.05$). During the initial stage of heating, no viscosity change is noted as hydration occurs at the molecular level within the granule. Once the hydration has reached the critical pasting stage, a rapid onset in the development of viscosity is observed. At this point, the structural changes in the granule are irreversible. Difference in pasting temperature indicates the varying accessibility of the granule to hydration (Murphy, 2000). UV irradiation causes some changes in the molecular structure, by reinforcing the granular structure of starch through some form of cross-linking (Gennadios, Rhim, Handa, Weller, & Hanna, 1998; Mark, Gaylord, Overberger, & Menges, 1986). These additional intermolecular bonds permit limited accessibility and hence increase the pasting temperature. When starch granules are grafted with AA, the hydrophilic –COOH groups counteract the water resistance effect of UV-induced cross-linkages and facilitate the hydration. Furthermore, the introduction of this pendant group to the backbone of the starch opens up the granule structure

Table 3
Pasting temperature, peak viscosity and peak time of native untreated sago, control and S-g-poly(AA) copolymers

| Sample | Pasting temperature (°C) | Peak viscosity (RVU) | Peak time (min) |
|---|---|---|---|
| Native untreated sago | 77.94$^{b}$ | 67.71$^{e}$ | 3.69$^{e}$ |
| Control (UV irradiated) | 80.09$^{a}$ | 111.36$^{d}$ | 3.89$^{d}$ |
| 2.5% AA | 78.98$^{b}$ | 114.36$^{d}$ | 3.97$^{c}$ |
| 5% AA | 79.11$^{b}$ | 153.69$^{c}$ | 4.20$^{b}$ |
| 7.5% AA | 78.49$^{b}$ | 166.88$^{b}$ | 4.35$^{a}$ |
| 10% AA | 78.56$^{b}$ | 188.96$^{a}$ | 4.22$^{b}$ |

The results are the averages of four replications.

Means with the same superscript denote no significant difference at the 5% probability level.

% AA indicates % of acrylic acid used in the graft copolymerization.

and exposes new hydroxyl groups which are available for intermolecular hydrogen bonding with water (Hari, Agarwal, & Garg, 1988).

From Table 3, it is observed that both the peak viscosity and peak time show similar trends. Control sample exhibited higher peak viscosity and peak time than native untreated sample ($p < 0.05$). Cross-linking caused by UV irradiation is believed to give additional intermolecular bonds that permit limited water accessibility and hence resulting in a gradual viscosity increase to maximum (Rutenberg, 1968). Likewise, the additional bonds also reinforce the strength of the starch granules and enable them to hold more water before rupture. This results in high peak viscosity. The UV-induced cross linkages are believed to be identical to the chemically-induced cross linkages and reinforce the hydrogen bonds in starch granules with additional bonds that act as bridges between molecules. When heated in water, the hydrogen bonds may be weakened or destroyed; however, the granule will be kept intact, to varying degrees, by the additional bridges (Wurzburg, 1986).

Peak viscosity and peak time of S-g-poly(AA) copolymers increase with increasing % of grafting ($p < 0.05$). Peak viscosity is also an indication of water holding capacity. Both starch and poly(AA) contain large numbers of hydrophilic groups in their structure, i.e., hydroxyl and carboxylic groups. The strong interchain hydrogen bonding which takes place between the grafted side chain of poly(AA) and the –OH groups of the starch backbone, enhances the water absorption ability of each component (Athawale & Lele, 2001). This is in agreement with the findings of this work, where peak viscosity increases with the % of AA grafted to the starch. When the water holding capacity increases, the duration required to swell until the rupture of starch granules will increase accordingly, thus leading to longer peak time with higher graft content.

Leach, McCowen, and Schoch (1959) reported slow swelling of thick-boiling hydroxyethyl milo starch. They explained that hydroxyethylation took place primarily in the more accessible intermicellar areas and, hence, sufficient micellar structures persist to hold the granule together and subsequently slow down the swelling process. Rutenberg (1968) also reported that when grafting was carried out without gelatinization of the starch (as in the case of this study), the linear fraction (amylose) of the polymer had not been grafted. It is presumed that, at the acrylic acid content studied in this work (2.5% to 10%), a great amount of linear fraction was still involved in micellar organization and not being grafted.

### *3.2.3. Breakdown, trough, setback and final viscosity*

This experiment (Table 4) showed that grafting of 2.5% of AA managed to retard the breakdown as compared to the rest of the samples ($p < 0.05$). On the other hand, when the amount of monomer was increased to 10%, breakdown was induced ($p < 0.05$). The control sample and other grafted copolymer showed insignificant difference ($p > 0.05$) from the native untreated starch. This indicated the ability of starch-grafted copolymer (2.5%) to withstand the heating and shear stress condition used in the testing. In another words, higher rigidity of the swollen granules has occurred (Zobel, 1984). Generally, most reports have shown that cross-linked starches are resistant to breakdown. The highly susceptible (to breakdown) property of 10% starch-g-poly(AA) copolymer requires further investigation. Similar behaviour was also found by John and Raja (1999) for cassava starch. The starch displayed

Table 4
Breakdown, setback, trough and final viscosity of native untreated sago, control and S-g-poly(AA) copolymers

| Sample | Breakdown | Setback | Trough | Final viscosity (RVA) |
|---|---|---|---|---|
| Native untreated sago | 46.50$^{b}$ | 14.33$^{e}$ | 21.21$^{f}$ | 35.54$^{e}$ |
| Control (UV irradiated) | 49.52$^{b}$ | 28.87$^{d}$ | 61.83$^{e}$ | 90.71$^{d}$ |
| 2.5% AA | 35.15$^{c}$ | 27.94$^{d}$ | 79.21$^{d}$ | 107.15$^{c}$ |
| 5% AA | 48.23$^{b}$ | 53.88$^{b}$ | 105.46$^{c}$ | 159.34$^{b}$ |
| 7.5% AA | 46.58$^{b}$ | 56.60$^{a}$ | 120.29$^{b}$ | 176.90$^{a}$ |
| 10% AA | 59.40$^{a}$ | 49.98$^{c}$ | 129.56$^{a}$ | 179.56$^{a}$ |

The results are averages of four replications.

Means with the same superscript denote no significant difference at the 5% probability level.

% AA indicates % of acrylic acid used in the graft copolymerization.

high single stage swelling and peak viscosity, but the swollen granules lacked ability to retain their structure and hence collapsed instantaneously. This reflects the weak nature of the inter- and intra-molecular hydrogen bonding of the starch copolymer. The high peak viscosity appears to predispose the gelatinized starch suspension to greater breakdown. As mentioned by Doublier, Llamas, and Le Meur (1987), there seems to be a relationship between swelling capacity and rheodestruction; the more swollen the starch granules, the more shear-sensitive the pastes become.

UV irradiation was found to induce setback, and this effect was found even more markedly after grafting with AA ($p < 0.05$). Nevertheless, when the AA was increased to 10%, the setback started to decrease ($p < 0.05$). The water repellent behaviour of S-g-poly (AA) is postulated to decline if more monomers are grafted onto starch. High graft content will reduce the linearity of the starch chain as well as increase the hydrophilicity. Thus, there is less retrogradation tendency. Aguilera and Stanley (1999) reported that the retrogradation of starch paste was affected by various factors, such as the source of the starch, the amylose: amylopectin ratio, the molecular weight, the linearity of the starch molecules, the time and temperature of cooling, the moisture content and the concentration of starch.

Generally, the high hot paste viscosities (trough) and final viscosities, for all treated samples ($p < 0.05$), are attributed to the high initial peak viscosity in the early stage of the pasting profile.

### 3.3. Swelling power and solubility

When starch is heated in excess water, the crystalline structure is disrupted and water molecules become linked by hydrogen bonding to the exposed hydroxyl groups of amylose and amylopectin. This causes an increase in granule swelling and solubility. Swelling power and solubility provide evidence of the magnitude of interaction between starch chains within the amorphous and crystalline domains. The extent of this interaction is influenced by the amylose/amylopectin ratio, and by the characteristics of amylose and amylopectin in terms of molecular weight/distribution, degree and length of branching, and conformation (Hoover, 2001).

Results obtained (Table 5) showed that UV irradiation caused certain extensive associating forces that suppressed the swelling of granules, as well as solubility when compared to native untreated starch ($p < 0.05$). The bonding forces within the starch granules play an important role in determining their manner of swelling (Leach et al., 1959). Restricted swelling and solubility were reported for rye starch granules (Radosta, Kettlitz, Schierbaum, & Christine, 1991). This is believed to be the consequence of the strong aggregative forces in the granular organization. This restriction may be overcome by introducing hydrophilic groups. Besides, restricted swelling and decreased WSI (water solubility index) values have also been reported for cross-linked waxy rice starch and waxy corn starch with 1% epichlorohydrin (Lii, Tsai, & Tseng, 1996).

Table 5
Swelling power and solubility of native untreated sago, control and S-g-poly(AA) copolymers

| Sample | Swelling power | Solubles (%) |
|---|---|---|
| Native untreated sago | $34.78^{a}$ | $46.36^{a}$ |
| Control (UV irradiated) | $16.09^{c}$ | $21.96^{bc}$ |
| 2.5% AA | $19.78^{b}$ | $26.67^{b}$ |
| 5% AA | $21.14^{b}$ | $20.06^{bc}$ |
| 7.5% AA | $20.55^{b}$ | $18.57^{c}$ |
| 10% AA | $21.96^{b}$ | $16.27^{c}$ |

The results are averages of triplicates.

Means with the same superscript denote no significant difference at the 5% probability level.

% AA indicates % of acrylic acid used in the graft copolymerization.

Grafting of AA monomer increases the swelling power but not the solubility. However, it should be noted that the swelling power of S-g-AA copolymer is still significantly ($p < 0.05$) lower than the native untreated one. This could be due to the low level of grafting used in this study, which is not sufficient to counteract the cross-linking effect of UV irradiation. The increased swelling power is attributed to the introduction of more hydrophilic groups (–COOH), such as in the preparation of hydrogel based on starch-g-AA (Athawale & Lele, 2001; Kiatkamjornwong et al., 2000). S-g-AA starch is expected to swell more if a higher amount of monomer is grafted onto the starch backbone. Li et al. (1986) reported that hydrogels based on saponified starch grafted with acrylic acid could absorb water up to 1998 g/g (as cited by Athawale & Lele, 2001). Gruber et al., and Masuda et al., (as cited by Athawale & Lele, 2001) had suggested that strong interchain hydrogen bonding takes place between the grafted side chain of poly(acrylic acid) and the hydroxyl groups of the starch backbone. Probably, hydrogen bonding favours the formation of a continuous and strong network which can hold more water in it.

Starch granules are insoluble in cold water. When heated in the presence of excess water, the amorphous regions that pervade the whole granule swell tangentially, forming a continuous gel phase. Young (1984) suggested that leaching occurs on swelling starch granules in water at temperatures of 57–100 °C. Mobile amylose molecules diffuse out of the swollen granule while the granule is intact, while most of the amylopectin remains hydrogen-bonded or crystallized in the granule residue. Results of the experiment have shown that UV irradiation reduced the amylose leaching (% of solubles) from the starch ($p < 0.05$). The difference in solubility behaviour between native untreated sago starch and control is noteworthy. Reduced solubility in the control starch indicates a close association or entanglement of the amylose with amylopectin components in the granules, and the cross-linking effect of UV treatment is most probably responsible for this. The insolubility is further enhanced when more AA is grafted onto the starch. The possible explanation could be that the grafting has taken place in the amylose molecules and hence immobilizes them. Together with the UV cross-linking effect, significant reduction in amylose leaching is therefore observed. This is particularly important in the formation of hydrogels (Athawale & Lele, 2001) whereby amylose swells in water and retains a significant fraction (>20%) of water within its structure, but does not dissolve in water.

The swelling and solubility properties of the S-g-AA copolymers are somehow different from the common native untreated starch behaviour. From the study of swelling and gelatinization of cereal starch, Tester and Morrison (1990) found that the amounts of leached total α-glucan and amylose were very highly correlated with the extent of starch swelling (higher swelling factor, higher leaching), which suggests a strong interdependence. In contrast, S-g-AA showed high swelling but low solubility when the degree of grafting increased.

Most published work reveals that the swelling behaviour of native untreated starch is primarily a property of the amylopectin content; amylose acts as an inhibitor of swelling, especially in the presence of lipids, when amylose–lipid complex tends to form (Sandhya & Bhattacharya, 1989; Tester & Morrison, 1990). Lii et al. (1996) suggested that the rigidity of starch granular structure might be proportional to its amylose content and inversely proportional to the degree of granular swelling. Since the same starch source was used in this study, variation in the amylose content is negligible. The possibility of different linear fraction contents, caused by photo-depolymerization/chain scission, is also absent, as shown by insignificant ($p < 0.05$) reduction of paste viscosity.

Some authors (Crosbie, 1991; Toyokawa, Rubenthaler, Powers, & Schanus, 1989) relate the greater swelling to higher peak paste viscosity. However, Konik, Mikkelsen, Moss, and Gore (1994) found no significant correlation between swelling power and RVA peak paste viscosity. It has also been reported that little or no relationship is observed between swelling power and Brabender pasting (Kulp & Lorenz, 1981). It should be noted that the native untreated sago starch exhibited greater swelling power but lower peak viscosity than treated starch.

## 4. Conclusions

From the FTIR analysis and carboxyl group content determination, UV-radiation curing was found to be successful in grafting acrylic acid onto starch. This

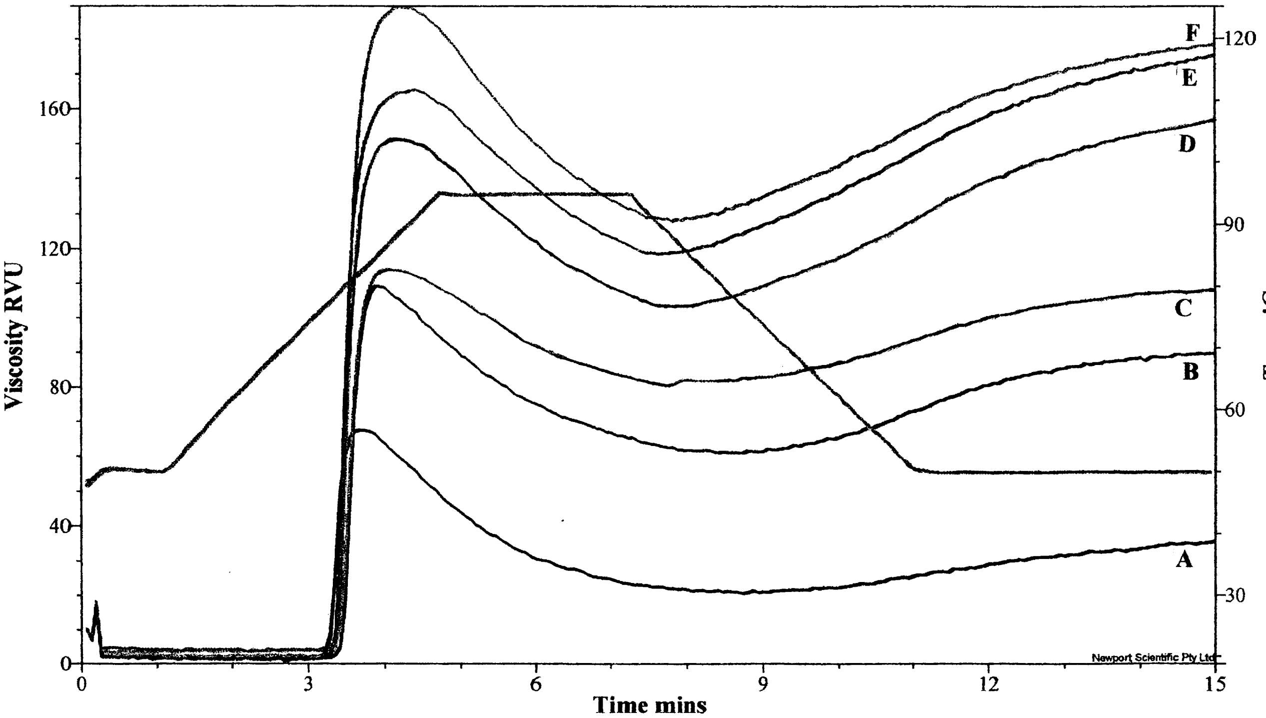

Fig. 3. RVA pasting curve for A (native untreated sago starch), B (control), C (S-g-AA, 2.5%), D (S-g-AA, 5%), E (S-g-AA, 7.5%) and F (S-g-AA, 10%).

provides a new alternative for graft copolymerization of starch with shorter preparation time than the conventional chemical-initiated methods.

UV irradiation and initiated grafting caused two major changes to the pasting profile of sago starch. First, UV irradiation caused cross-linking in sago starch, resulting in restrained granule hydration, high pasting temperature, high peak viscosity and high setback. Secondly, grafting of AA monomer favoured the formation of a three-dimensional hydrophilic network that counteracted the limited hydration effect of UV irradiation and increased water-holding capacity. However, the low % of AA used in this work was not sufficient to retard setback. Generally, the UV dosage used in this work was considered low and insufficient to induce any depolymerization of starch (Tomasik & Zaranyika, 1995; Fiedorowicz, Tomasik, You, & Seung-Taik, 1999). This was evident by insignificant ($p < 0.05$) reduction of paste viscosity after UV irradiation (Bertolini, Mestres, & Colonna, 2000).

The overall profiles of the paste viscosity curves for all treated samples, were not significantly changed (Fig. 3). This shows that the original starch granule structure has not been altered. After irradiation and grafting, the starch was fully recovered from the reaction mixture in granular form without any morphological change during the treatment.

The cross-linking effect of UV irradiation retarded the swelling and solubility of sago starch. Grafting of AA increased the swelling power while maintaining the low solubility. There seems to be no relationship between the peak paste viscosity and swelling power of the starch samples studied. In conclusion, the changes in the swelling and solubility of S-g-AA were mainly due to the alteration of configuration brought about by the UV grafting treatment. Further investigation into UV-initiated graft copolymerization conditions, such as the effect of % photoinitiator, dosage of radiation, and higher % of monomer, may be necessary to provide better information for understanding this photografting system.

## Acknowledgements

We would like to express appreciation to the Sarawak Government for a research grant and Universiti Malaysia Sabah for sponsoring and allowing JSL to pursue Ph.D. studies.

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