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Flow behaviour of sago starch-g-poly(acrylic acid) in distilled water and NaOH—effect of photografting

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Abstract

Flow behaviour study of UV initiated sago starch-g-poly(acrylic acid) (AA) was carried out to elucidate the effect of UV irradiation and photografting on native sago starch. The flow behaviour of native and treated sago starch in different gelatinizing agent (distilled water and NaOH) was also investigated. All starch samples exhibited pseudoplastic characteristic and fitting to Herschel–Bulkley model. Flow behaviour of all samples were highly dependent on the UV treatment, degree of grafting and type of gelatinizing solvent, whereby the volume fraction of the granules varies in accordance with the swelling capacities as well as resistances to rupture. As a result, control sample imparted highest viscosity when distilled water was used as solvent; on the other hand, 20 AA imparted highest viscosity when NaOH was used as solvent. Swollen granule fractions affect the viscosity magnitude of the flow behaviour of a starch sample as evident by photomicrographs.

Keywords: Photografting; Starch-g-poly(acrylic acid); Gelatinization

1. Introduction

Flow behaviour is part of starch paste rheological study besides the viscoelastic properties. Flow behaviour measurement may reveal flow behaviour of materials which leads to improved efficiency in processing and helps formulator or end users to decide the type of starch which is optimal for their individual needs. A study of the rheological properties of the starch pastes also enables the engineering scale up in production (Jackman, 1991; Islam, Azemi, & Manan, 1997), quality control as well as improvement of final products (Race, 1991). Characterizing flow behaviour of a polysaccharide such as starch enables researchers to establish a relationship between the micro-structural processes and the macroscopic behaviour.

Application of starch (such as thickeners, sizing and coating papers, sizing textile, adhesive formulations and other applications) always involve gelatinization of starch, that breaks the inter-chains hydrogen bonding so as the rheological properties of starch paste can be utilized effectively (Solorza-Feria, Jiménez-Aparicio, Arenas-Ocampo, & Bello-Pérez, 2002). Gelatinization of starch induces a complex structural modification, leading to dramatic apparent viscosity changes. Depending upon the degree to which starch granules are swollen and the extent of solubility, a wide range of properties can be exhibited. According to Launay, Doublier, and Cuvelier (1986), rheological behaviour of starch systems would depend upon:

1. the volume fraction occupied by the dispersed phase (swollen granules);
2. the viscoelastic properties of the dispersed (soluble) phase;
3. the rheological properties of the continuous phase; and
4. the interactions between dispersed and continuous phases.

UV curing technique was employed to produce sago starch-g-poly(acrylic acid) (S-g-PAA) in this study. The introduction of hydrophilic poly(acrylic acid) (PAA) to sago

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starch backbone would alter the conformation and granular structure of starch granules. Water is generally used in food application for gelatinization of starch, however, in non-food applications, such as in adhesives and corrugated cardboard industry, alkali gelatinization of starch is of great importance. The objectives of this study are, first, to explore the effect of UV irradiation and UV photografting on flow behaviour of sago starch; and second, to examine the effect of different gelatinizing agents (namely distilled water and NaOH) on the flow behaviour of both native sago starch and the grafted starch.

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 from Ciba Specialty Chemicals, Singapore. Acrylic acid (AA) (Fluka, > 99% purity) was used as received without further purification. Other chemicals are of analytical reagent grade and water was glass distilled.

2.2. Synthesis of S-g-PAA

Twenty millilitres of distilled water was added into 0.4 g (2% of starch weight) of photoinitiator (Irgacure 2595) The mixture was heated (90–95 °C) to dissolve the photoinitiator and then cooled before adding in 20 g of sago starch and the required amount of AA (5, 10 and 20% of starch on dry basis). Starch was dispersed in the solution by vigorous stirring using spatula and poured immediately in a 18 cm × 8 cm × 0.1 cm glass plate. The solution was spread evenly and UV curing was performed by passing the glass plate under a M200U2 UV IST lamp ($\lambda = 180–450$ nm, 200 W/in.) at a speed of 5 m/min. After curing, modified starch was washed five times with hot boiling ethanol (85%) to remove the homopolymer (Bayazeed, Elzairy, & Hebeish, 1989). Each washing was carried out for 15 min while the starch slurry was agitated by magnetic stirrer. Lastly, the starch copolymer was centrifuged and dried overnight at 70 °C. Starch sample was then ground to 0.2 μm using a hammer mill (Glen Greston, England, Type: DCFH 48). Control sago starch was prepared under identical procedures without the monomer AA. S-g-PAA synthesized with 5, 10 and 20% AA is represented as 5AA, 10 AA and 20 AA, respectively, in the text.

2.3. Determination of carboxyl content (–COOH)

The carboxyl group content was determined according to the procedure of ISO 11214 by International Starch Institute (ISI, 1998).

2.4. Flow behaviour measurement

Flow behaviour measurement was carried out on starch samples gelatinized with two solvents, namely deionised water and 0.025 N NaOH. The required amount of starch samples were weighed into a screw-cap 100 ml conical flask and top up with deionised water/0.025 N NaOH to a total of 30 g. The mixture solution was then heated on a hot plate while stirring with a magnetic bar. When the starch suspension turned from opaque to translucent solution, the flask was immediately transferred into a water bath at 95 °C and held for 15 min. After that, the flask was transferred to a water bath preset at 80 °C for another 10 min for full viscosity development. The samples were held at 80 °C throughout the experiment to prevent gelation. Each sample was prepared fresh and measured within short duration to avoid evaporation as well as alkaline hydrolytic in sample prepared with NaOH. The flask was tightly screwed with the cap to prevent evaporation from taken place during heating and holding.

Steady shear data were obtained using a Carri-Med Csl^2 100 Controlled Stress Rheometer (TA Instruments, Florida, USA) attached with a stainless steel 4 cm diameter 2° angle cone and plate geometry. Shear rate was increased logarithmically in a continuous ramp mode. Torque was fixed at logarithmic ramp to minimize the inertia effect of the rheometer.

A pipette cut to a tip diameter of 5 mm was used to reduce shearing during sampling. The starch solution was loaded on the plate and the cone was lowered into the sample. Expelled materials were trimmed off. The sample at the edge of the cone–plate system was covered by silicon oil to prevent drying. Pre-shear was also performed to eliminate any shear history of the sample. Sample was allowed to rest for 300 s after compression in order to restore structure that might have been disturbed. For effect of temperature and concentration, each sample was sheared from 5 to 1000 s^{-1} for 120 s and subsequently returned to the initial rate. Each sample was duplicated and two measurements were obtained from each replicate to obtain the mean value. All measurements were carried out at 25 °C.

2.5. Light microscopic examination

A light microscope (Olympus, BH-2) fitted with a crossed polar analyzer was used to observe the starch in deionised water/0.025 N NaOH before and after gelatinization. The samples were gelatinized according to the sample preparation procedure of flow behaviour study. Starch paste was stirred before sampling using a wire loop and transferred onto a microscope slide. The sample was covered with slip and sealed using varnish to prevent dehydration, and samples were viewed under phase contrast attachment and photographed with a camera (Olympus). All samples were observed under magnification of 200 × and 400 ×.

2.6. Statistical analyses

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

3. Results and discussions

From Table 1, the percentage of carboxyl group (–COOH) increases with the increasing amount of AA% in the grafting process. This is a very general trend which has been found in other grafting systems (Bayazeed et al., 1989; Fang, Lu, Wang, & Fang, 1996; Gao, Tian, Yu, & Duan, 1994; Mostafa, 1995; Rahman et al., 2000; Singh & Ray, 1997). During the grafting process, monomer continuously diffuses into the polymer matrix. The ability of starch macroradicals to capture AA would depend on the availability of AA molecules in their vicinity; as it is understandable that the active centres on starch molecules, i.e. starch macroradicals are immobile. The increase in AA% will therefore lead to an increase in the degree of grafting. As the amount of AA used in the preparation is low, the degree of grafting is generally low.

3.1. Flow behaviour

Herschel–Bulkley Model is found best fitting all the sample flow curves data with the regression coefficients ranging from 0.9942 to 0.9998. Therefore, it has been used to explain the flow behaviour of all starch samples under studied. Data taken during the descending segment of the shear cycle are used for flow characterization and estimates of the Herschel–Bulkley parameters (Rao, Okechukwu, Da Silva, & Oliveira, 1997; Rao & Tattiyakul, 1999).

3.1.1. Water as gelatinizing agent (steady shear data)

Fig. 1 shows the flow curves for native sago starch, control, 5 AA, 10 AA and 20 AA gelatinized using distilled water. Sample concentration used was 5% (w/w). Basically, all samples exhibit a non-Newtonian shear-thinning (pseudoplastic) behaviour, which is a curvature downwards on the shear rate axis (Fig. 1), with flow behaviour index, $n < 1$ (Table 2). In pseudoplastic flow, an increase in shear rate results in more rapid flow or reduced viscosity. It is interesting to find that native, control (UV irradiated) and 5 AA starch pastes display hysteresis loops (Fig. 1). However, it should be noted that the hysteresis loop for 5 AA is at the opposite direction with control and native sago starch with 'up' curve being lower than 'down' curve. 'Up' curve refers to the shear stress imposed by fluid with increasing shear rate, whereas 'down' curve is the shear stress responded to decreasing shear rate. This 'anticlockwise' shear stress and shear rate loop is one of the indications of shear thickening (antithixotropic) characteristics (Dintzis, Berhow, Bagley, Wu, & Felker, 1996). Flow behaviour during the shear cycle of both 10 AA and 20 AA seem to be time independent, with both 'up' and 'down' curves almost overlapping.

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

Sample	% COOH[a]
Native sago	–
Control (UV irradiated)	–
Five AA	0.61 ± 0.002
Ten AA	0.98 ± 0.010
Twenty AA	1.50 ± 0.065

[a] % COOH is based on dry basis. The results are the average and the standard deviation of duplicate.

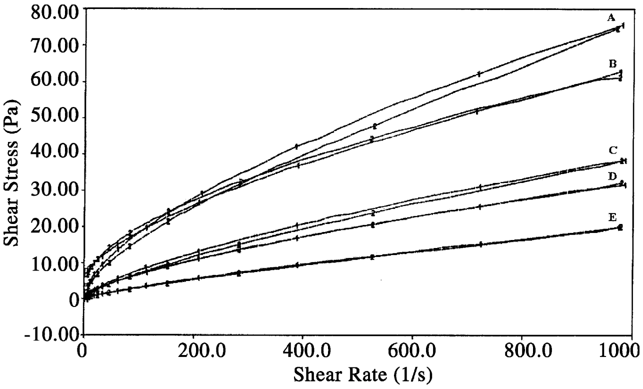


Fig. 1. Flow curves for five different starch pastes gelatinized with distilled water. (1) represents 'up' curve and (2) represents 'down' curve. A, control; B, 5 AA; C, native sago starch; D, 10 AA; E, 20 AA.

The flow behaviour of starch pastes appeared closely bound to the starch structure in the pastes. The starch paste could be regarded as a blend of swollen granules, pieces of disrupted granules and starch molecules liberated from the granules and then solubilized; the ratio of these different fractions varied. Viscosity of starch dispersion is strongly influenced by swelling of starch granules and the granules' integrity (Borwankar, 1992; Tattiyakul & Rao, 2000). In distilled water, the order of decreased viscosity under increasing shearing rate was: control >5 AA > native sago > 10 AA > 20 AA. Our previous study (unpublished data) found that UV irradiation induces cross-linking in sago starch, which in turn reduces the swelling power and solubility in distilled water. Also, with increasing degree of grafting, another photografting induced cross-linking becomes predominant and restricts the swelling power, solubility and gelatinization in distilled water.

At 5% AA, the cross-linkages brought about by UV irradiation and photografting behave like chemically induced cross-links located randomly within granules, just enough to stabilize the granules and hence, strengthen the relatively tender swollen starch granules (Tattiyakul & Rao, 2000). Control sample due to UV induced cross-linking, also exhibits higher apparent viscosity than native sago

Table 2
Effect of sample treatment on Herschel–Bulkley parameters

Sample	Yield stress (τ_y) (Pa)		Consistency coefficient (K) (Pa s^n)		Flow behaviour index (n)	
	H_2O[a]	NaOH[a]	H_2O	NaOH	H_2O	NaOH
Native sago	0.27 ± 0.08c	0.13 ± 0.01d	0.20 ± 0.02d	0.05 ± 0.005c	0.80 ± 0.01b	0.84 ± 0.02a
Control	1.51 ± 0.09b	0.33 ± 0.02c	0.60 ± 0.01b	0.14 ± 0.02b	0.70 ± 0.01c	0.76 ± 0.001a
Five AA	3.92 ± 0.33a	0.14 ± 0.004d	1.02 ± 0.08a	0.05 ± 0.003c	0.58 ± 0.01e	0.82 ± 0.005a
Ten AA	0.13 ± 0.03c	0.42 ± 0.02b	0.33 ± 0.04c	0.13 ± 0.02b	0.67 ± 0.01d	0.79 ± 0.01b
Twenty AA	0.01 ± 0.006c	2.03 ± 0.03a	0.07 ± 0.01e	0.64 ± 0.002a	0.82 ± 0.01a	0.67 ± 0.002b

Flow behaviour measurement was carried out at 25 °C. The results are mean and the standard deviation of four measurements. Means with the same alphabet in the same column denotes no significant difference at the 5% probability level.

[a] H_2O-sample gelatinized with distilled water at 95 °C, 5% (w/w); NaOH-sample gelatinized with 0.025 N NaOH at 95 °C, 3% (w/w).

starch ($P < 0.05$). As shown in Fig. 1, 5 AA exhibits higher shear resistance than control at lower shear rate ($< 100\ s^{-1}$); somehow the trend reverses at much higher shear rate ($> 100\ s^{-1}$). This may suggest that 5 AA paste is less stable and sensitive to high shearing effect. Native sago starch imparts lower viscosity than control and 5 AA ($P < 0.05$), as indicated by the consistency coefficient, K (Table 2). It is postulated that under the severe cooking condition during preparation, native starch granules which lack of inter- and intra-molecular cross-linking most probably experienced partial granules rupture before being subjected to shearing, due to their fragility as compared to control and grafted starches.

The very low viscosities exhibited by 10 AA and 20 AA ($P < 0.05$) may be explained by restricted gelatinization due to formation of extensive covalent bonds in the starch granules (photografting induced cross-linking); which in turn limit the water accessibility and swelling capacity. The different degree of grafting has induced dramatic change in the swelling characteristics and hence, the rheological properties of sago starch. In fact, qualitative observation during sample gelatinization suggests incomplete gelatinization as evident by the presence of sediment and phase separation of the starch pastes.

3.1.2. NaOH as gelatinizing agent

As comparison, another set of experiment using NaOH as solvent was carried out NaOH with higher ionizing ability than water is expected to facilitate the hydration of both 10 AA and 20 AA, dissolve the starch granules and enhance the gelatinization. By doing so, the grafted starch granules will be able to swell freely and contribute differently to the flow characteristics. Flow curves of these five samples gelatinized using 0.025 N NaOH is shown in Fig. 2. S-g-PAA copolymers (especially 20 AA) exhibit very high viscosity when gelatinized in alkali at 5% (w/w); for ease of handling, the concentration of starch samples to be gelatinized with alkali was reduced to 3% (w/w). Similarly, all samples are characterized by pseudoplastic behaviour with clockwise hysteresis loops. However, the order in terms of shear stress (implication of viscosity) was different; follows the decreasing order of 20 AA > control and 10 AA > native sago and 5 AA. Again, the thixotropy (area of hysteresis loop) is found decreasing in the same order. It is interesting to note that the curvature becomes less pronounced for both native and 5 AA, indicating their lower shear-resistant character.

As shown in both Figs. 1 and 2, NaOH as solvent imparts dramatic change in the apparent viscosity of starch graft copolymers. The presence of NaOH increases the starch granules affinity to water, induces swelling and results in significant increment in granule size. Starch gelatinization in NaOH involves both chemical and physical mechanism (Ragheb, Abd El-Thalouth, & Tawfik, 1995) and all samples in this study seemed fully gelatinized by exhibiting clear and translucent pastes. Evans and Haisman (1979) pointed out that the mass fraction granules play an important role in the magnitudes of rheological properties. In this study, the interpretation of starch pastes flow behaviour is focused more on the basis of swelling capacities as described by Evans & Haisman (1979) and Wong and Lelievre (1982). This is because UV irradiation and photografting significantly reduce the solubility of sago starch and hence it is presumed that the continuous phase with less solubilized starch components may be of less important role as compared to the dispersed phase. However, it should be emphasized that the contribution of continuous phase to the starch rheology should not be totally neglected. There is

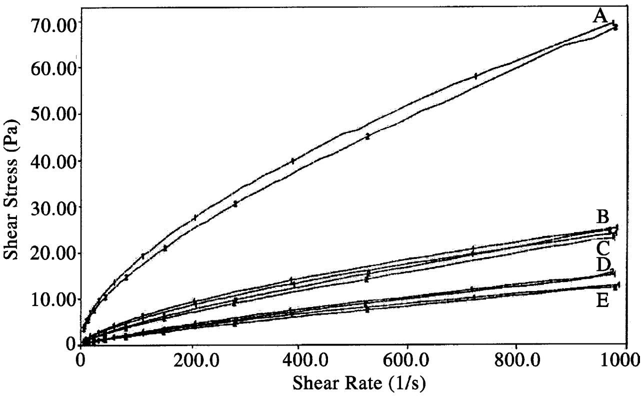


Fig. 2. Flow curves for five different starch pastes gelatinized with 0.025 N NaOH. (1) represents 'up' curve and (2) represents 'down' curve. A, 20 AA; B, control; C, 10 AA; D, native sago; E, 5 AA.

empirical evidence that suggests that suspension viscosity increases with the volume fraction occupied by the starch granules. At low volume fraction, the granules are relatively apart, with little interaction. However, as volume fraction increases, inter-granular interactions become important, with suspension viscosity showing a greater dependence on volume fraction (Okechukwu & Rao, 1998).

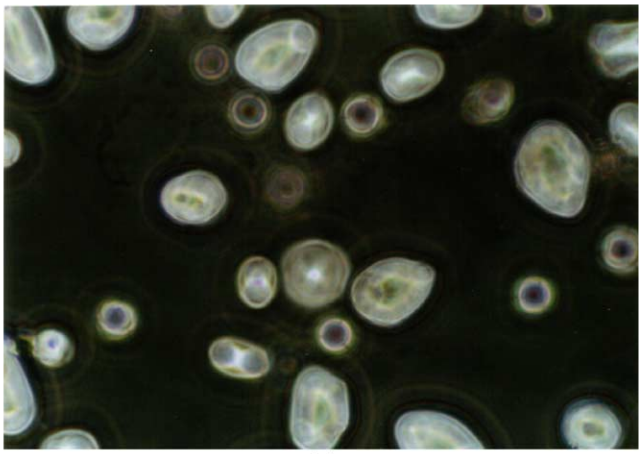
In alkali, 20 AA is fully hydrated and imbibes solvent to expand to the maximum swelling volume and causes highest flow resistance ($P < 0.05$) to the shear (Table 2). Adding of base such as NaOH enables some ionization to occur, providing sodium counter-ions and the polymeric ion. As more and more of the carboxyl groups on the grafted polymer branch become ionized, mutual repulsion of the charges forces the polymer chain to uncoil and assume a more nearly rod like configuration with a resultant increased resistance to flow and increased solution viscosity (Glavis, 1968). The highly viscous paste of 20 AA may also be attributed to the intermolecular hydrogen bonding that encourage the molecular association (thickening effect) as implies by its low coil overlap concentration (unpublished data). Table 2 shows that flow behaviour index (n) value for 20 AA gelatinized in NaOH is smaller than the counter part gelatinized in distilled water; an opposite trend from other samples. It is anticipated that in 20 AA, those granules with high degree of grafting (not all granules being grafted as photografting is a random process) exert greater extent of swelling in NaOH than ungrafted granules, and increase the standard deviation of granule size distribution in the starch dispersion. The increased of these two factors were reported to lower the flow behaviour index (n) by Okechukwu and Rao (1995, 1996a,b).

Glavis (1968) also explained that addition of more sodium hydroxide may results in build-up of sodium counter-ions and hence a repression of the effective ionization of the PAA polymer chain. The effect is some chain coiling and a consequent reduction in solution viscosity. This is may explain the lower apparent viscosities of 5 AA and 10 AA than 20 AA, where the PAA side chains (with –COOH functional groups) are shorter and less for neutralization with NaOH. The apparent viscosities of control is higher than native, this verifies the presence of UV induces cross-linkages within the control granules.

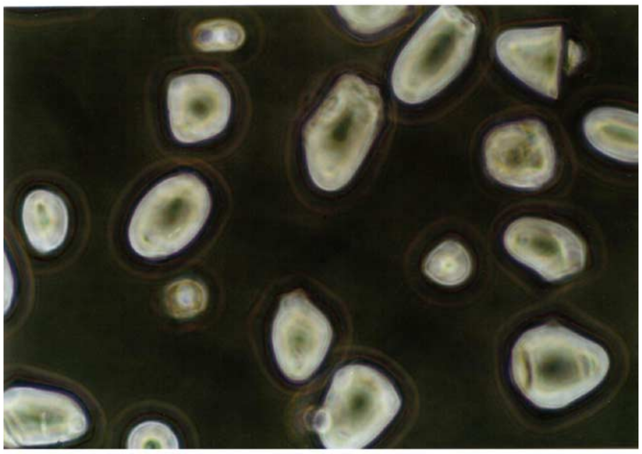
Starch samples gelatinized either by distilled water or NaOH show the yield stress (τ_y). Occurrence of yield stress (τ_y) observed at low shear rates has been widely reported (Christianson & Bagley, 1984; Evans & Haisman, 1979). Sopade and Kiaka (2001) also reported the presence of yield stress on six varieties of sago starch samples. The yield stress is found highly correlated to the apparent viscosity; in which high yield stress is always associated with high K (consistency coefficient). High K and τ_y value are mainly due to the existence of interactions between swollen granules and/or between swollen granules and an extra granular network of exudates (Miller, Derby, & Trimbo, 1973). This in turn means that the structural elements formed by molecular interactions (Whistler & BeMiller, 1997) that resist the flow are more when the viscosity of one starch pastes is high. The present investigation is in agreement with previous finding (Christianson & Bagley, 1984) that τ_y values depend on the extent of swelling of starch granules.

3.2. Light microscopic examination

The examination of photomicrographs present additional/supporting evidence of the different evolution of native and treated starch granules prepared by different solvent, that contribute to the above rheological properties and granular size distributions. Fig. 3 shows photomicrographs of native sago starch dispersions in distilled water and 0.025 N NaOH before gelatinization under phase contrast. In the presence of NaOH, sago starch granules exhibit rapid and greater swelling at room temperature as proven by the bigger granular size. When viewed under polarized light (Fig. 4), all native starch granules appear to shine while exhibiting a dark 'Maltese cross', this symbolizes



(a)



(b)

Fig. 3. Phase contrasted photomicrographs of native sago starch in (a) distilled water and (b) NaOH at room temperature. Photographs were magnified by 400 ×. (Scale bar: 9 cm = 170 μm).

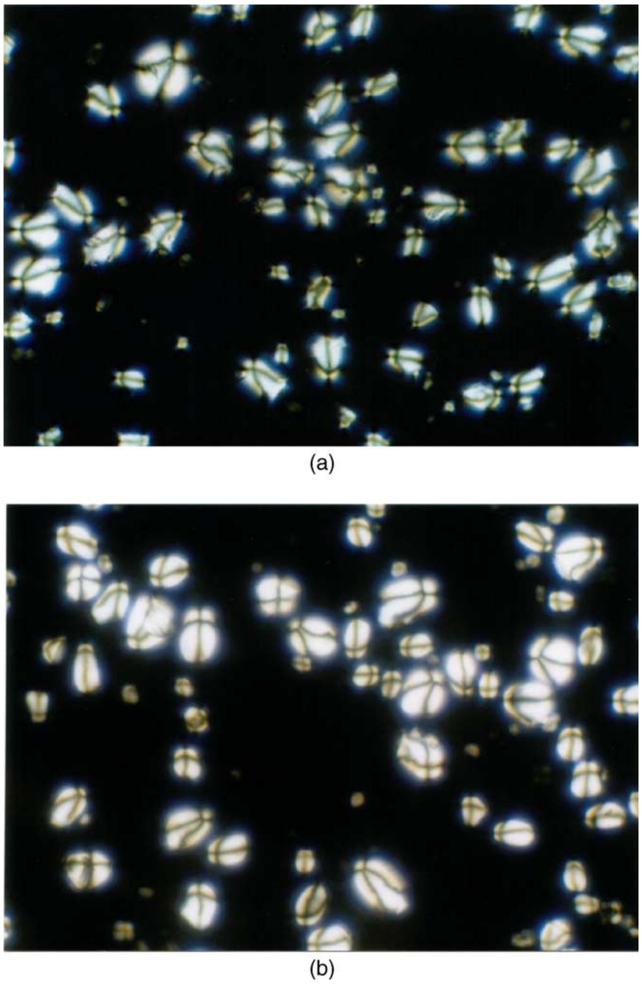


Fig. 4. Native sago starch in (a) distilled water and (b) NaOH at room temperature viewed under polarized light. Photographs were magnified by 200 × . (Scale bar: 2 cm = 75 μm).

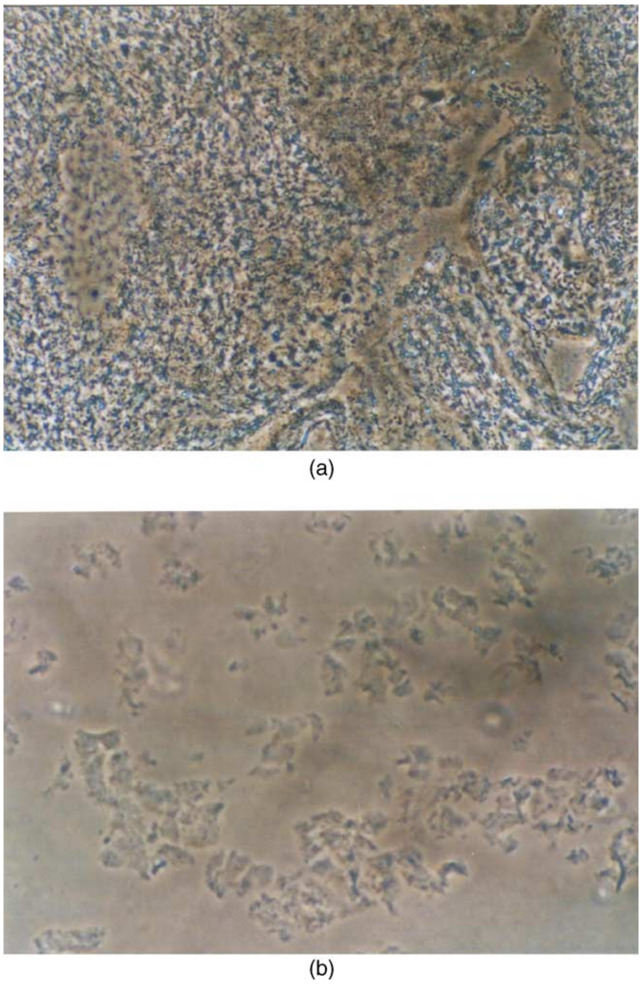


Fig. 5. Native sago starch gelatinized in (a) distilled water and (b) NaOH. Photographs were magnified by 200 × . (Scale bar: 2 cm = 75 μm).

the birefringence. This indicates that the ordered structure of starch granules is unaltered without heating. From Fig. 4, it is clearly shown that starch granules are having bigger size, with more swollen and round shape.

By referring to the photographs of Figs. 5–7, the effect of different gelatinizing solvent used for native sago starch, control and 20 AA can be easily compared. Native sago starch upon gelatinization in distilled water is fully ruptured, leaving remnants of the granular materials dispersed in the continuous matrix. When gelatinized in NaOH, a more homogeneous solution with relatively less granular remnants is observed, suggesting that NaOH dissolves most of the starch components when coupled with heating. Besides that, NaOH may also impart base hydrolysis (Ragheb, Adb El-Thalouth, & Tawfik, 1996) on starch granules which may shorten the chain length of starch molecules. Native sago starch is unable to maintain the granular integrity under both preparation procedures. This strongly supports the reason given earlier for its low apparent viscosity in flow behaviour.

After gelatinization, control sample pasted in distilled water consists of highly swollen granules crowding with each others (close-packing). The appearance of ridges of unknown nature is observed on the surface of all swollen granules (Fig. 6a). The ridges may seem to limit the further expansion or extensive swelling of the granules. This may well suggest the UV irradiation induces contraction (by cross-linking) effect on starch granules as found earlier (unpublished data). In NaOH (Fig. 6b), the strong dissolution and hydrolytic action disrupts most of the granules, leaving more structured remnants of granules as compared to native sago starch. Some of the relatively resistant granules seem to preserve the granular structure and integrity, although swell extensively (compared to in distilled water). The ridges on the surface somehow disappear in the presence of NaOH. The granular structure of 20 AA is found intact with no ridges observed after heating in distilled water (Fig. 7a), though some swelling has been taken place; suggesting the UV irradiation induces cross-linkages are different from the photografting induces cross-linkages. The photografting induces cross-linkages are stronger and able to sustain the effect of NaOH by maintaining the granular structure and integrity (Fig. 7b).

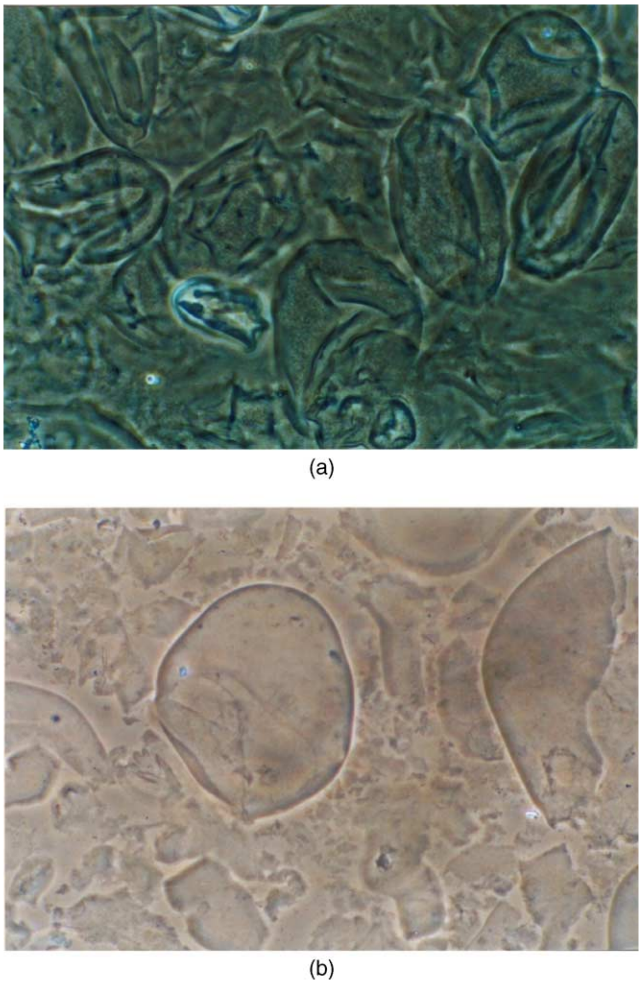


Fig. 6. Control (UV irradiated) gelatinized in (a) distilled water and (b) NaOH. Photographs were magnified by 200 × . (Scale bar: 2 cm = 75 μm).

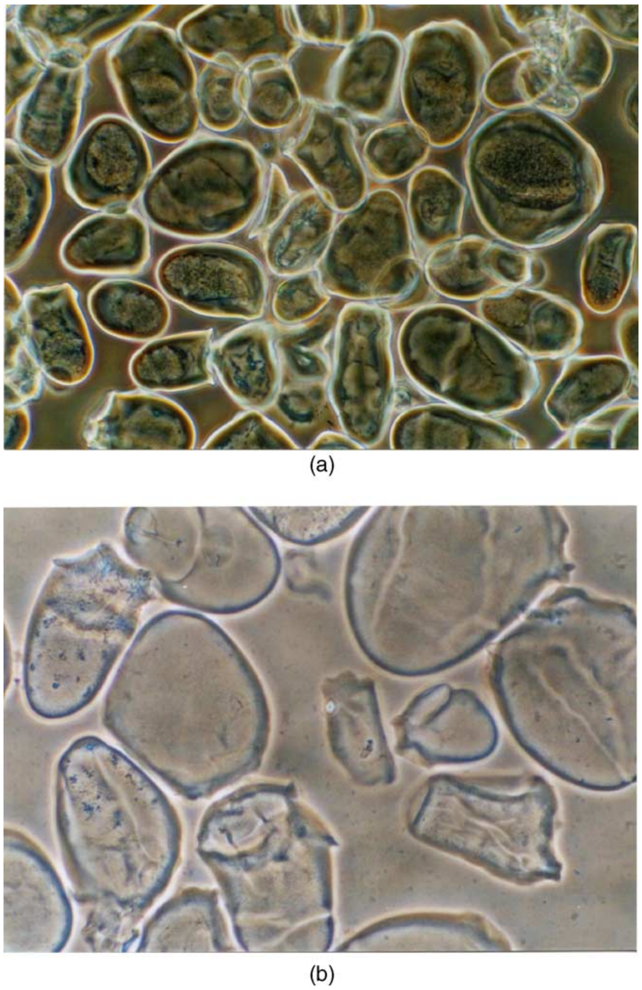


Fig. 7. 20 AA gelatinized in (a) distilled water and (b) NaOH. Photographs were magnified by 200 × . (Scale bar: 2 cm = 75 μm).

The above interpretation of flow behaviour from the aspect of granular volume causes by swelling capacity seems in agreement with the equivalent data of these photomicrographs, in which the bigger the granular volume, the higher the viscosity is. The utilization of different gelatinizing agents (distilled water and NaOH) provides better insights for the physical and chemical alterations of sago starch induced by UV irradiation and UV photografting of PAA.

4. Conclusions

Flow behaviour of native sago starch and treated starch are highly depend on the type of solvent used to gelatinize the samples, whereby the volume fraction of the granules varies in accordance with the swelling capacities as well as resistances to rupture. The effect of UV irradiation and different degree of grafting are reflected in the resistance to rupture, ease of gelatinization as well as maximum swelling ability when heated in different solvent as evident by the microscopic examination. Swollen granule fractions play a major role in the viscosity magnitudes of flow behaviour. Effect of sample concentration, temperature and shear rate on flow behaviour were also carried out and will be reported in another paper.

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