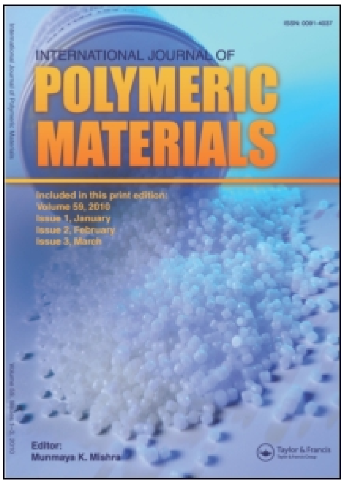

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Modification of sago starch by graft copolymerization. Effect of reaction conditions on grafting parameters

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MODIFICATION OF SAGO STARCH BY GRAFT COPOLYMERIZATION. EFFECT OF REACTION CONDITIONS ON GRAFTING PARAMETERS

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Graft copolymerization of acrylonitrile onto sago starch was carried out by a free radical initiating process in which the ceric ion (Ce^{4+}) was used as an initiator. The reaction conditions significantly influence the graft copolymerization. The percentage of grafting, grafting efficiency and rate of grafting were all dependent on the concentration of ceric ammonium nitrate (CAN), acrylonitrile (AN), sago starch (AGU, anhydro glucose unit), mineral acid (H_2SO_4) and the reaction temperature and period. The optimum yield was obtained when the concentrations of CAN, AN, AGU and H_2SO_4 were used at 9.61×10^{-3}, 0.653, 0.152 and 0.187 mol L^{-1}, respectively. The optimum temperature and reaction period were 50°C and 90 min, respectively. The rate of graft copolymerization was examined using the experimental results and the reaction mechanism. The polya1crylonitrile grafted sago starch was characterized by using FT-IR spectroscopy, DSC and SEM analysis.

Keywords: graft copolymer, sago starch, free radical, acrylonitrile, polyacrylonitrile

INTRODUCTION

Scientists are exploring ways to use starch as a replacement for petroleum-derived polymers in an effort to generate new markets for

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surplus starch and to increase the biodegradability of plastic articles. Combining starch with synthetic polymers through graft polymerization is one of the best approaches for achieving these goals. Graft polymerization of methyl acrylate onto starch gives materials that can be processed into tough and flexible plastic articles [1]. Because it is low in cost, renewable and biodegradable, starch is an attractive filler for higher-cost biodegradable polymers. The treated starch has better adhesion to the polymer, and the properties are improved compared to untreated starch. The use of grafted starch gives stronger materials with enhanced water resistance. Graft copolymerization of vinyl monomers onto starch is an excellent method for preparing composites of starch with synthetic polymers [2, 3]. Grafting has been utilized as an important technique for modifying physical and chemical properties of polymers. Graft copolymerization of starch and other natural macromolecules can be initiated by transition metal ions and Ce^{4+} was widely used in the modification of cellulose, fiber, starch *etc*. [4, 5]. Redox system generally comprises transition metal ions, which occur in various oxidation states [6]. Such oxidized metal ions may directly oxidize starch and the free radicals are produced onto starch to initiate the graft copolymerization. In this present study, we have optimized the reaction of graft copolymerization of acrylonitrile onto sago starch using ceric ion as an initiator, and the study will later be extended to biodegradability test for plastic materials.

EXPERIMENTAL

Materials

Sago starch was obtained from Tepung Sago Industries Ltd (Malaysia). It was dried at 60°C for 48 h before use. Acrylonitrile monomer was purchased from Merck Company, and the acrylonitrile was passed through columns filled with chromatographic grade alumina. Ceric ammonium nitrate (BDH), methanol (Beaker) and other chemicals used were of analytical reagent grade.

Graft Copolymerization

The starch slurry was prepared from 2.50 g of sago starch and 100 ml distilled water in a 250 ml three-neck flask equipped with a stirrer and condenser. The reactions were carried out in a thermostat water bath and N_2 gas was injected into the flask to purge it from oxygen. The starch slurry was preheated at 80°C for about 30 min with stirring. After the starch gelatinized, the flask content was cooled to 50°C temperature and then 2.0 ml diluted H_2SO_4 (water: H_2SO_4; 1 : 1) was added to the reaction mixture. About 5 min later, the required ml of 0.1 M CAN was added and 10 min later the required amount of acrylonitrile monomer was added to the mixture. The reactions were carried out for specific hours and after completion of the reaction the flask was cooled under running tap water. The product was poured into 300 ml methanol to induce precipitation. The products were washed several times with methanol–water (4 : 1) and dried at 50°C to a constant weight.

Extraction of Homopolymer and Determination of Extent of Grafting

Exactly 2.000 g crude products of polyacrylonitrile (PAN) grafted sago starch were taken in a flask and extracted with DMF using a soxhlet extractor for 12 h to remove PAN homopolymer. Then the pure product was dried at 50°C to a constant weight [7].

The percentage of grafting, grafting efficiency and rate of graft copolymerization were determined using the equations of Vijayakumar et al. [8]

$$\text{Percentage of grafting} = \frac{\text{weight of grafted polymer}}{\text{weight of backbone}} \times 100$$

$$\text{Grafting efficiency} = \frac{\text{weight of grafted polymer}}{\text{weight of grafted polymer} + \text{weight of homopolymer}} \times 100$$

$$\text{Rate of grafting} = \frac{\text{weight of grafted polymer}}{(\text{M.W. of monomer}) \times (\text{reaction time/sec}) \times (\text{volume/ml})} \times 1000\,(\text{molL}^{-1}\text{sec}^{-1})$$

Side-Chain Separation

The PAN side-chain was removed from the sago starch backbone according to the procedure described by Reyes et al. [9]. Exactly 1.00 g of PAN grafted sago starch and 100 ml of 1 M HCl solution were placed in a 250 ml one neck flask. The flask was fitted with condenser and the mixture was refluxed for 6 h. The warm mixture was filtered and the solid was washed with distilled water, 2.5% NaOH, distilled water, 50% acetic acid, distilled water and methanol. The isolated PAN side-chain was dried at 50°C to a constant weight.

Analysis of FT-IR Spectra

Infrared spectra of the polymer samples were obtained in an FT-IR spectrometer (Perkin-Elmer, 1725), from KBr pellets of sago starch, polyacrylonitrile grafted sago starch and side-chain PAN.

Differential Scanning Calorimetry Analysis

Differential scanning calorimetry (DSC) experiments were carried out by Polymer Laboratories differential scanning calorimeter with N_2 flow rate at $50\,\mathrm{ml\,min^{-1}}$. The DSC thermograms were obtained from powder samples of sago starch and PAN grafted sago starch, which were packed into aluminum pans and heated at rate of $10\,\mathrm{K\,min^{-1}}$.

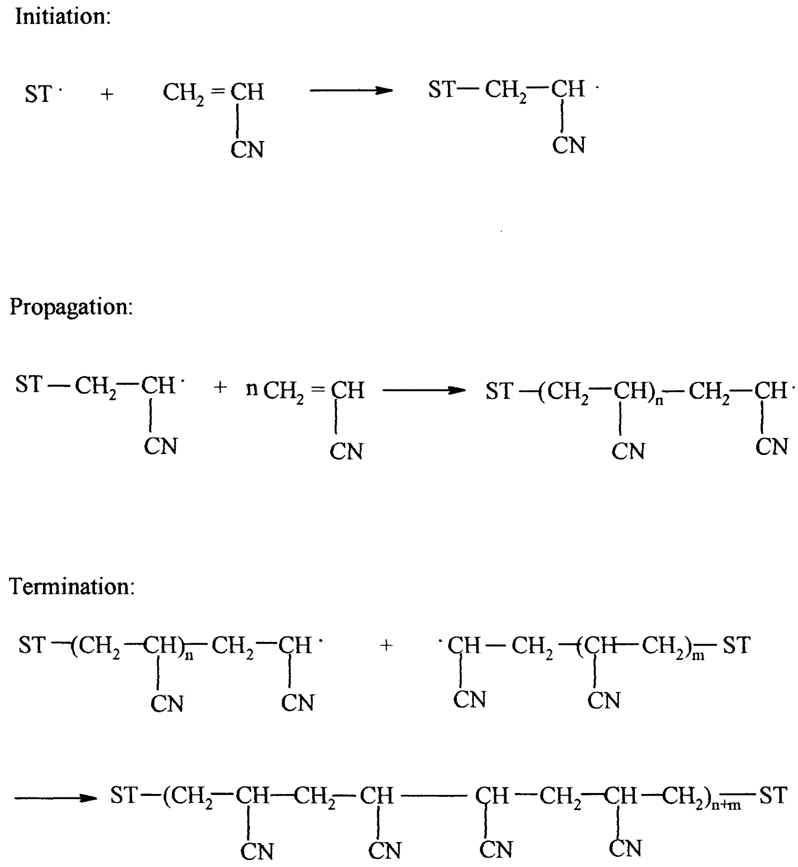
RESULTS AND DISCUSSION

Reaction Mechanism

The cerium ion attacks the starch molecules and forms a starch-ceric complex. The Ce^{4+} ion in the complex is then reduced to Ce^{3+} ion and a hydrogen atom is oxidized. Consequently, a free radical is formed on the starch, while the bond is broken between carbon atoms 2 and 3 of the glucopyranose unit. The free radical formation onto starch molecule (AGU) was presented in our earlier paper [10]. The polymeric starch free radical is formed onto starch molecule and then reacts with acrylonitrile (AN) monomer to initiate graft copolymerization. In the presence of AN monomer, the starch free radical was added to the double bond of the monomer resulting in a covalent bond between monomer and starch to initiate chain reaction. Subsequent addition of AN molecules to the chain increases the size of the branched chain. Termination of the graft copolymerization is through combination of two radicals. The overall reactions are given in Scheme 1, where ST is free radical of sago starch molecule and the structure of starch molecule with free radical is presented elsewhere [10].

Analysis of FT-IR Spectra

Figure 1a shows the infrared spectrum of sago starch in which the bands of starch at $3402\,\mathrm{cm^{-1}}$ and $1646\,\mathrm{cm^{-1}}$ are due to O–H stretching and bending modes, respectively. Additional characteristic bands were observed at $2930\,\mathrm{cm^{-1}}$ and $1024\,\mathrm{cm^{-1}}$ are due to C–H stretching and bending, respectively. The infrared spectrum of purified PAN grafted sago starch is shown in Figure 1b. The characteristic absorption band



SCHEME 1

of nitrile at 2244 cm^{-1}, due to presence of C≡N stretching appear in addition to the absorption bands of sago starch. The presence of C≡N group on the purified grafted sago starch indicates that PAN has successfully grafted onto sago starch.

Effect of Reaction Temperature

Four different temperatures (30, 40, 50 and 60°C) were used for grafting reaction and the effect of temperature on the percentage of grafting is shown in Table 1. The highest percentage of grafting, 50.46%, was observed at 50°C temperature. This temperature attained the optimum yield of grafted copolymer. Beyond 50°C the grafting decreased. With the increase in temperature more and more radicals

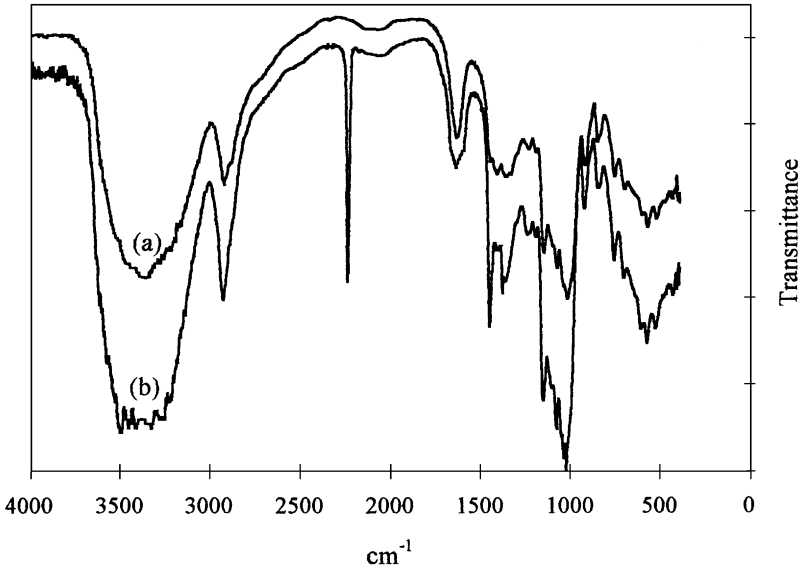


FIGURE 1 FT-IR spectrum of (a) sago starch, (b) polyacrylonitrile grafted sago starch.

were formed, which increased the extent of grafting. However, increase in temperature beyond specific limit causes as increased extent of radical termination, reducing the graft level. The decrease experienced in grafting at higher temperature has been attributed to

TABLE 1 Effect of Reaction Conditions on the Grafting Parameters[a]

Effect of temperature		Effect of acid concentration		Effect of reaction period	
Temperature[b] (°C)	% of grafting	$[H_2SO_4]$[c] (mol L^{-1})	% of grafting	Reaction period[d] (min)	% of grafting
30	20.14	0.050	40.12	30	35.10
40	36.55	0.092	50.46	60	55.12
50	50.46	0.187	55.12	90	60.10
60	39.40	0.401	42.51	120	55.12

[a] Concentration of [AGU], [AN] and [CAN] were 0.152 mol L^{-1}, 0.653 mol L^{-1} and 4.59×10^{-3} mol L^{-1} respectively.

[b] Other conditions: Reaction period, 60 min and $[H_2SO_4]$, 0.092 mol L^{-1}.

[c] Other conditions: Temperature, 50°C and reaction period, 60 min.

[d] Other conditions: Temperature, 50°C and $[H_2SO_4]$, 0.187 mol L^{-1}.

the instability of the initiator, particularly CAN, at elevated temperature, and increased rate of termination [11].

Effect of Acid Concentration

The effect of H_2SO_4 concentration on the percentage of grafting is shown in Table 1. The optimum percentage of grafting, 55.12%, was achieved when the concentration of H_2SO_4 used was $0.187\,\mathrm{mol\,L^{-1}}$. The use of mineral acids in the grafting process assists in the enhancement of graft level and acts as a catalyst in the hydrolysis of starch, leading to uncoiling of the chains and improving the monomer accessibility [12]. However, at higher acid concentration, decreases in grafting were attributed to a corresponding reduction in the ceric-starch complex formation as well as increase in the termination rates. It has also been speculated that the increase in termination may be due to an abundance of hydrogen protons, which act as free radical terminators [11].

Effect of Reaction Period

The yield of grafting reached a maximum of 60.10% at 90 min. Beyond this period grafting decreased (Table 1). Perhaps this is because the available sites for grafting on the starch backbone decreased after 90 min and with the viscosity of the reaction system getting higher it was difficult for monomer molecules to reach the sites [4]. Another possible explanation for the leveling off of grafting levels with time is the reduction in the number of sites available for grafting [11].

Effect of Initiator Concentration

The effect of initiator concentration on the yield of grafting was significant and the grafting increases with the increase of CAN concentra tion from 2.54×10^{-3} to $9.61 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ (Figure 2). The highest percentages of grafting and grafting efficiency were achieved, 63.01% and 93.8% respectively, when the ceric ion concentration was used at $9.61 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$. The percentages of grafting and efficiency decreased above a CAN concentration of $9.61 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$. The decrease of graft level at higher concentration of CAN may be due to the efficiency of Ce^{4+} taking part in the termination of growing grafted chain and homopolymerization [13]. The decrease in grafting yield at higher initiator concentration could be due to a decrease in the rate of polymerization. A significant increase in the initiator concentration beyond $9.61 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ not only facilitates the more active center on the backbone but also facilitates the homopolymerization.

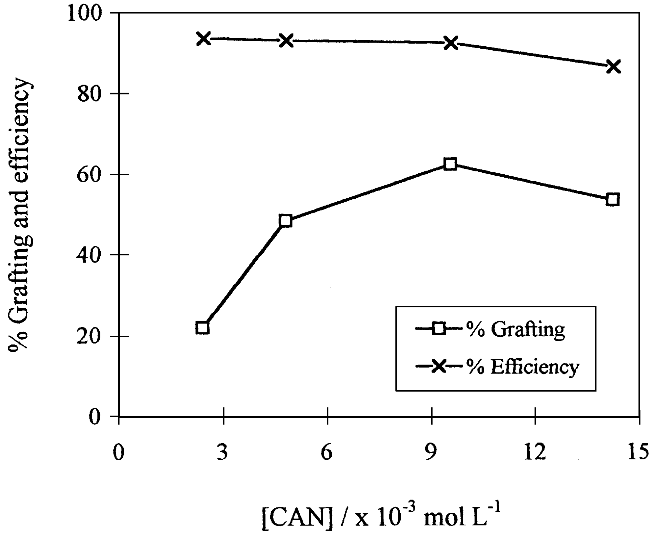


FIGURE 2 Effect of initiator [CAN] concentration on % of grafting. Temperature, 50°C; [AN], 0.653 mol L^{-1}; [AGU], 0.152 mol L^{-1}; reaction period, 90 min; [H_2SO_4], 0.187 mol L^{-1}.

Effect of Monomer Concentration

The effect of monomer concentration on the grafting yield is shown in Figure 3. The percentage of grafting increases with the increase of monomer (AN) concentration from 0.315 mol L^{-1} to 0.653 mol L^{-1}. The percentage of grafting and grafting efficiency reached a maximum, as 83.04% and 95.9% respectively, at 0.653 mol L^{-1} AN concentration. The effect of monomer concentration on the grafting is a gel effect, which arises from the solubility of homopolymer in the monomer itself. A contribution of this effect would be pronounced at higher monomer concentration. As a result of this effect the termination rate decreased. Besides this, the gel effect helped in swelling the starch, which ultimately facilitates the diffusion of monomer to the active sites on the starch backbone, thereby enhancing the grafting level [3]. At higher monomer concentration beyond 0.653 mol L^{-1}, the percentage of grafting decreased because of the higher percent of homopolymer were formed in the starch-graft-polyacrlonitrile. One expected reason might be that swelling of the base polymer at higher monomer concentration was not favorable for grafting.

The relation between rate of grafting and monomer concentration is presented in Figure 4. It was found that when AN increased from

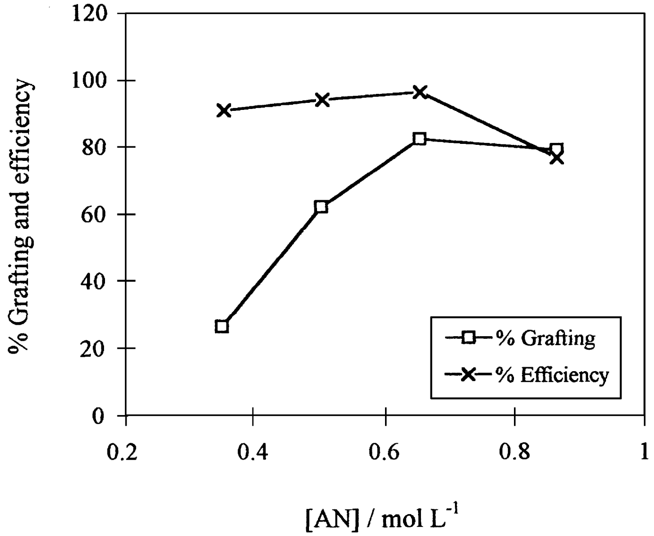


FIGURE 3 Effect of monomer [AN] concentration on % of grafting. Temperature, 50°C; [CAN], 9.61×10^{-3} mol L^{-1}; [AGU], 0.152 mol L^{-1}; reaction period, 90 min; [H_2SO_4], 0.187 mol L^{-1}.

0.315 to 0.653 mol L^{-1} the rate of grafting increased linearly and then decreased beyond 0.653 mol L^{-1}. At higher monomer concentration, the rate of grafting was found to decrease (deviated point omitted in Figure 4) and this is due to the formation of more homopolymer in the system. Reyes et al. [9] investigated the grafting of acrylonitrile monomer to wheat starch by ceric ion and they achieved maximum 26% of grafting copolymer product. In this study, we obtained the maximum percentage of grafting and efficiency were 83.04% and 95.9%, respectively. Therefore, a significant yield of grafting was obtained at the present study.

Differential Scanning Calorimetry Analysis

Differential scanning calorimetry (DSC) gives significant information. The DSC curves of sago starch and polyacrylonitrile (PAN) grafted sago starch are presented in Figure 5. An endothermic transition was observed at 324°C for sago starch sample. Whereas PAN grafted sago starch exhibited exothermic transition at 288°C. A new exothermic transition in the PAN grafted sago starch was observed which is probably due to the enhancement of interaction between the nitrile groups of grafted copolymer and the hydroxyl groups in the sago

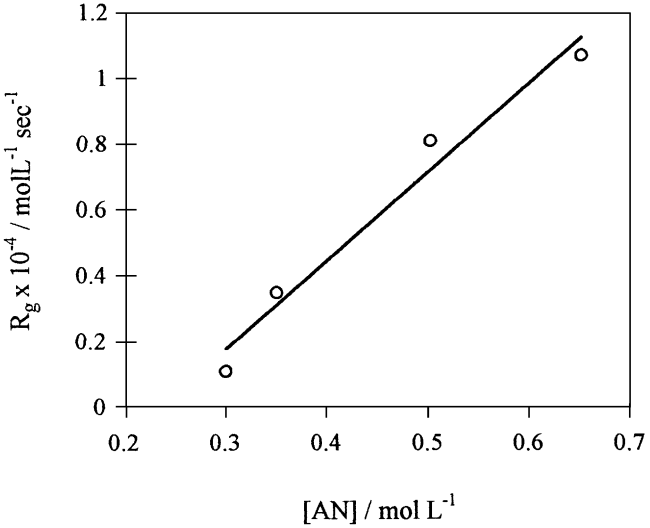


FIGURE 4 Effect of monomer [AN] concentration on the rate of grafting. Other conditions as in Figure 3.

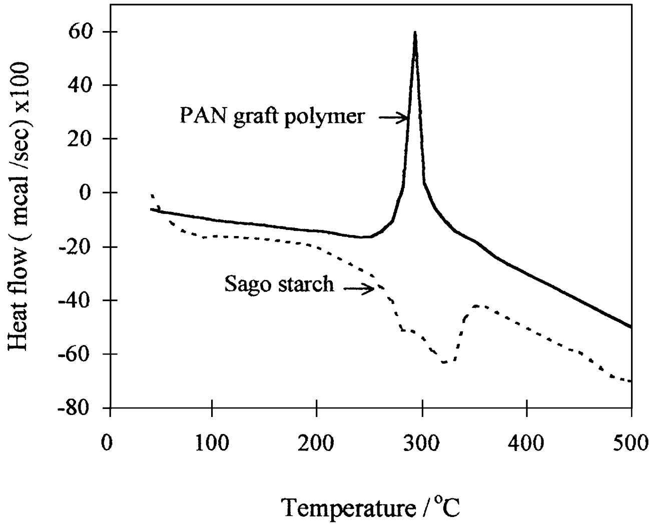


FIGURE 5 DSC Thermograms of polyacrylonitrile grafted polymer and sago starch. Plot of heat flow (mcal sec^{-1}) versus temperature.

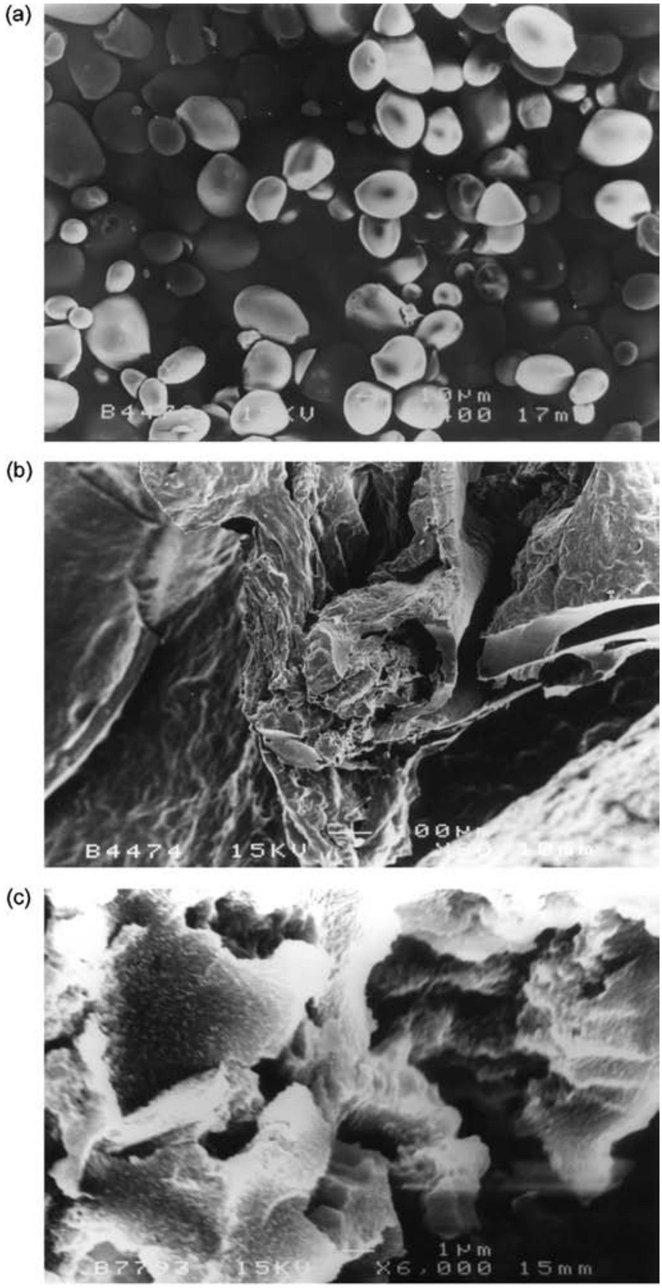


FIGURE 6 SEM photograph of (a) sago starch, (b) gelatinized sago starch, and (c) polyacrylonitrile grafted sago starch.

starch backbone. This result confirmed that grafting occurred of polyacrylonitrile onto sago starch.

Scanning Electron Microscopy Analysis

Sago starch, gelatinized sago starch and PAN grafted sago starch were imaged by scanning electron microscopy (SEM) as shown in Figures 6(A, B, C). The sago starch under SEM possesses a particle shape called deformed prolate ellipsoid (Figure 6A). The gelatinized starch has a smooth and compact surface, which might be caused by the formation of amorphous structure after the gelatinization (Figure 6B). After the graft formation, the smooth and compact surface of amorphous structure disappeared in Figure 6C. The PAN grafted copolymer shows that the grafting process occurred homogeneously on the surface of the starch, which changes the surface morphology in Figure 6C. The SEM analysis reasonably supported the assumption that grafting occurred onto sago starch backbone.

CONCLUSION

Polyacrylonitrile grafted sago starch was prepared from acylonitrile monomer and sago starch. The effect of reaction conditions was found to be significant in the graft copolymerization. The optimum yield of grafting, grafting efficiency and rate of graft polymerization were all dependent upon the concentration of CAN, AN, AGU, H_2SO_4, as well as the reaction temperature and period, and a significant yield of grafting was observed in this study.

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