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Synthesis and characterization of multi-active site grafting starch copolymer initiated by $KMnO_4$ and HIO_4/H_2SO_4 systems

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ABSTRACT

A novel initiator system containing KMO_4, HIO_4, and H_2SO_4 for synthesizing grafting starch copolymers is reported. In this system, $KMnO_4$ was used to oxidize the primary hydroxyl group to aldehyde group of glucose in the starch, and the formed aldehyde group reacted with Mn^{4+}, Mn^{3+} to afford starch free radical. At the same time HIO_4 perform as the oxidant to open the C2—C3 bond of glucose ring in starch to form two more aldehyde groups, and then two more free radicals are generated. As a result one glucose unit could provide ultimately three active sites for starch grafting reaction. Graft copolymers with a higher grafting ratio and grafting efficiency could be obtained by using the composite initiation system than the $KMnO_4/H_2SO_4$ initiation system. The grafting of polyacrylamide onto the corn starch backbone was confirmed by viscometry, elemental analysis, infrared spectroscopy, nuclear magnetic resonance, X-ray diffraction and scanning electron microscopy.

1. Introduction

Starch is an inexpensive, biodegradable, and renewable resource, and has therefore been considered as a promising candidate for developing sustainable materials. Due to its structure and properties, including poor water solubility at room temperature, gelatinization at high temperature, and high viscosity, the applications of starch are limited. To realize the full potential of starch, it must be modified chemically (Zhou, Jia, Cui, & Xie, 2009; Duan, Lv, Yan, Hou, & Gong, 2012; Yin, 2001). Currently, modification of starch is typically carried out by initiating copolymerization at reactive centers in the molecular backbone of starch using chemical (Li, Zhao, Zhang, & Xue, 2007) or physical means (Lv et al., 2013; Yu, Huang, Yu, & Zou, 2013). The monomers used in starch graft co-polymers are predominantly vinyl compounds such as acrylonitrile (Navarchian, Sharafi, & Kermanshahi, 2013; Apopei, Dinu, & Drăgan, 2012), acrylic acid (Witono, Noordergraaf, Heeres, & Janssen, 2012; Bardajee & Hooshyar, 2013), acrylamide (AM) (Sorour et al., 2013; Xu, Ding, & Teng, 2011; Nakason, Wohmang, Kaesaman, & Kiatkamjornwong, 2010), acrylate (Wu & Zhou, 1993), and styrene (Sheikhn, Akhavan, & Ataeivarjovi, 2013; Kaewtatip & Tanrattanakul, 2008). The typical initiators or initiation systems used for synthesis of starch graft copolymers include cerium salt (Mino & Ksizerman, 1958), hydrogen peroxide–ferrous ion system (Li, Zhu, & Jin, 2010), persulfate (Lanthong, Nuisin, & Kiatkamjornwong, 2006; Willett & Finkenstadt, 2006), potassium permanganate (Mostafa, Samarkandy, & El-Sanabary, 2011) and manganic pyrophosphate (Gao, Tian, Yu, & Duan, 1994). Ceric ammonium nitrate (Liu, Cheng, Wu, & Ma, 1993; Kutsevol, Guenet, Melnik, Sarazin, & Rochas, 2006) is one of the most widely used

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initiators for grafting polymers onto starch. This initiator has low activation energy, less triggering time, high grafting efficiency, and good reproducibility when compared to other initiators. However, its industrial application is limited because of the high price of cerium ions. The superfluous initiators in case of hydrogen peroxide-based initiation system can be easily eliminated without any threat to the environment, and it is inexpensive when compared to cerium ammonium nitrate. However, the low grafting efficiency and the generation of excess homopolymer restrict its widespread application. When compared with that of ceric ammonium nitrate, the oxidizing ability of persulfate is weaker, the rate of reaction is lower, the reaction time is longer, and the reaction temperature is higher. Therefore, a low-cost and high-efficiency novel initiator is needed for grafting free-radical initiated vinyl polymers onto starch. Study of the initiation mechanism by potassium permanganate shows that the initiator initially oxidizes primary hydroxyl on the starch backbone to aldehyde groups and is itself reduced to manganese dioxide. Free radicals are easily produced on starch when the aldehyde groups in the starch molecules interact with tri- or tetravalent manganese ions. Wang, Yu, Gao, Zhang, and Tian (1998) have investigated the ability of $KMnO_4$ to initiate graft copolymerization on corn starch, dialdehyde starch and hypochloric oxidation starch, and have shown that grafting to dialdehyde starch is easiest amongst the three. This indicates that it is critical to generate aldehyde groups on starch to affect graft copolymerization initiated by $KMnO_4$. When a large number of aldehyde groups are present on the starch molecule, the grafting is efficient. The reagent HIO_4 selectively oxidizes vicinal diols to dialdehydes and, in the process, breaks the C—C bond. The high specificity of HIO_4 to oxidize both the hydroxyls on the C_2—C_3 of starch molecules to aldehyde groups, and simultaneously break the C_2—C_3 bond leads to the formation of the dialdehyde starch (Jacson & Hudson, 1937; Jacson & Hudson, 1938). Sloan, Hofreiter, Mellies, and Wolff (1956) have investigated the reaction conditions for oxidizing starch with HIO_4 and the properties of the oxidized starch. He, Shen, and Liu (2004) have proposed a method of preparation of dialdehyde starch with the use of virtual homogeneous phase system, wherein the reaction conditions are mild, and uniform oxidizability is ensured. Zheng, Yao, He, and Zheng (1996) have prepared dialdehyde starch wherein the oxidation by HIO_4 gave a product that had approximately 60% of its diols that oxidized. Similarly, Lan, Liao, Xie, Wei, and Huang (2002) prepared dialdehyde starch with HIO_4; the content of dialdehyde in tapioca starch was 87%. All these observations indicate that HIO_4 can oxidize starch to efficiently generate aldehyde groups. On the basis of the above study, it has been proposed that the two adjacent secondary hydroxyls in the C_2—C_3 position of the glucose ring of the starch molecule are oxidized by periodic acid to two aldehyde groups. Therefore, a maximum of three active sites can be produced in a single glucose ring in the starch molecules, which consequently, indicates an increase in the grafting efficiency. In this paper, a novel binary mixture of potassium permanganate and periodic acid in the presence of sulfuric acid is used as an initiator in the graft copolymerization of starch.

2. Experimental

2.1. Materials

The native, granular corn starch (maximum moisture content = 14.0%, maximum ash = 0.15%, pH range of 5.4–6.4) used as the polymer substrate was obtained from a starch factory of Luoyang, China. AM, used as the monomer, was supplied by TianJin Development LeTai Chemical Co., LTD, China. Potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4), and periodic acid ($HIO_4{\cdot}2H_2O$) were obtained from Beijing Chemical Works, China. Sodium hydroxide, ethylene glycol, and glacial acetic acid were analytical grade.

2.2. Synthetic procedure

Corn starch (4.0 g), dried in an oven for 24 h, was added to distilled water (70 mL) in a three-necked flask. The mixture was mechanically stirred at 65 °C or 80 °C for 30 min to obtain an ungelatinized or a gelatinized starch, respectively. The gelatinized starch was then cooled down to 65 °C. After that, the mixture was stirred under a nitrogen atmosphere throughout the reaction. Then, potassium permanganate (0.15 mmol) and periodic acid (0.11 mmol) were added into the container. After 10 min, the monomer, AM (4.0 g), was added to the reaction solution. Finally, the pH of the solution was adjusted to 1 with sulfuric acid. After 3 h, the solution was neutralized with sodium hydroxide. After deposition, washing, filtration, and drying, we obtained the crude starch graft co-polymerization product. The dried crude product was suspended in a mixture of ethylene glycol:glacial acetic acid (4:6, v/v), stirred for 24 h, washed with ethanol or acetone three times, filtered, and dried to obtain the pure graft product.

2.3. Calculation of grafting parameters

Monomer conversion ratio, α (%), percentage of grafting ratio, G (%), and percentage of grafting efficiency, E (%), which were used to show the level and efficiency of grafting reaction, were calculated as shown in Eqs. (1), (2), and (3), respectively:

$$\alpha\ (\%) = \frac{(W_1 - W_0)}{W_n} \times 100, \tag{1}$$

$$G\ (\%) = \frac{(W_2 - W_0)}{W_0} \times 100, \tag{2}$$

$$E\ (\%) = \frac{(W_2 - W_0)}{(W_1 - W_0)} \times 100, \tag{3}$$

where W_0 is the weight of corn starch (g), W_1 is the weight of crude graft product (g), W_2 is the weight of pure graft product (g), and W_n is the weight of AM monomer (g). The calculations for the grafting parameters were similar to that reported by Ge, Xu, Zhang, Lu, and Ye (1999) and Yang, Cao, Liu, and Ma (2004).

2.4. Measurement of the viscosity of crude product

Dried crude graft product (6 g) and distilled water (100 mL) were mixed together and stirred for 1 h at 95 °C. The viscosity of the solution was determined with a rotary viscometer (Shanghai SHENSHENG, NDJ-79, China).

2.5. Characterization

2.5.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of corn starch, polyacrylamide, and graft co-polymers were recorded from the KBr pellet in the range from 4000 cm^{-1} to 400 cm^{-1} using a FTIR spectrometer (Nicolet, MAGNA-IR 560 E. S. P., USA).

2.5.2. Elemental analysis

An elemental analyzer (ANTEK, ANTEK 9000, USA) was used to analyze starch graft co-polymerization products obtained after initiation with either potassium permanganate or potassium permanganate/periodic acid.

2.5.3. Scanning electron microscopy

Scanning electron microscopy (SEM; FEI, Guanta 200F, USA) was used to investigate the surface morphology of corn starch, oxidized

Table 1
Effect of reaction temperature on graft copolymerization[a].

Reaction temperature (°C)	Crude product (g)	Homopolymer (%)	*E* (%)	Viscosity (mPa s)	Color of product
50	8.1351	13.8	72	45	Brown
60	8.1473	14.6	71	37	Brown
65	8.3711	12.5	76	24	White
70	8.2878	8.0	85	15	White

[a] Reaction conditions: starch to AM ratio, 1:1; [$KMnO_4$], 0.15 mmol; pH, 1; reaction time, 3 h.

Table 2
Effect of amount of periodic acid on graft copolymerization under ungelatinization[a].

HIO_4 (mmol)	Crude product (g)	Homopolymer (%)	*E* (%)
0	8.3711	12.5	76
0.10	8.5108	10.0	81
0.15	8.7316	8.6	84
0.20	7.9347	9.0	82

[a] Reaction conditions: starch to AM ratio, 1:1; [$KMnO_4$], 0.15 mmol; pH, 1; graft reaction temperature, 65 °C.

starch, and starch-g-PAM products obtained after the initiation of the co-polymerization by potassium permanganate or potassium permanganate/periodic acid.

2.5.4. X-ray diffraction

X-ray diffractometer (XRD; Bruker, D8 ADVANCE, Germany) with Cu*K*α radiation and a Ni filter was used to detect the crystalline structure of corn starch, gelatinized starch graft co-polymer obtained from the reaction at 90 °C, and ungelatinized starch graft copolymer obtained from the reaction at 65 °C. The voltage and the current were 40 kV and 40 mA, respectively.

2.5.5. Nuclear magnetic resonance

Nuclear magnetic resonance (^{13}C MAS NMR; Bruker, AV-300, Switzerland) studies were conducted to confirm grafting of the monomers onto starch and the mechanism of $KMnO_4$ and $KMnO_4/HIO_4$ initiation systems. The rotational speed, the relaxation delay time, and the scan times were 12 kHz, 5 s, and 2000–3000, respectively.

3. Results and discussion

3.1. Effect of reaction temperature on graft copolymerization

The solution of corn starch in distilled water was stirred at different reaction temperature for 30 min, and then nitrogen gas was allowed to flow through the mixture to remove the air within. After adding $KMnO_4$ and then stirring for 10 min, AM monomer was added. A certain amount of H_2SO_4 was added to adjust the pH value of the solution (pH = 1), the total volume of the mixture was 100 mL. The effect of reaction temperature on *E* (%) and viscosity of the product is shown in Table 1.

The co-polymers are prepared at four different reaction temperatures (50, 60, 65, and 70 °C) while all the other parameters of the reaction are unchanged, i.e., a fixed reaction time of 3 h, a fixed ratio of starch: AM, a pH of 1, and the concentration of $KMnO_4$ at 0.15 mmol. The solution color for the reactions conducted at 50 °C and 60 °C is brown and ungelatinized, which indicates that the graft co-polymerization reaction is not effective at low temperatures. At 65 °C and 70 °C, the solution turns white at the end of the reaction (Table 1, entries 3 and 4). The ungelatinized form of starch is granular where the initiator produced reactive sites only on the surface of starch. Therefore, fewer active sites are created and the utilization of initiator is also low. This results in a portion of initiator remaining in the solution even after the completion of the reaction, making the solution brown. At higher temperature, the starch would be gelatinized, its molecular structure is destroyed. In aqueous solutions, the starch completely unfolds when it swells and absorbs water, and the initiator is able to produce multiple active sites on the molecular structure of starch. This ensures a higher utilization of the initiator and a higher production of free radicals in starch. Therefore, *G* (%) and *E* (%) are higher in the gelatinized starch rather than the ungelatinized starch. At 70 °C, some of starches gelatinize. There is 9% increase in *E* (%) when the reaction is performed at 70 °C compared to its value at 65 °C, and the viscosity of graft product drops by 9 mPa s for the reaction at 70 °C. The result shows that with the increasing of reaction temperature, content of homopolymers and viscosity of products was decreased, but the percentage of grafting efficiency, *E* (%), was increased. The phenomenon of the weight of crude products is more than the total weight of corn starch and monomer (8 g), it is probably due to initial oxidation of primary hydroxyl to aldehyde on the starch by initiator. Some of the aldehyde groups become free radicals which grafted with AM, the other was further oxidized to carboxyl. Therefore the weight of oxidized starch was higher than the native starch, which resulted in increasing of the weight of the crude products.

3.2. Effect of periodic acid on graft copolymerization

3.2.1. Effect of periodic acid on graft copolymerization under ungelatinization

The solution of corn starch in distilled water was stirred at 65 °C for 30 min, and then nitrogen gas was allowed to flow through the mixture to remove the air within. After adding $KMnO_4$ (0.15 mmol) and HIO_4 (0–0.2 mmol) for 10 min, AM monomer (4.0 g) was added. The Effect of periodic acid on graft copolymerization is shown in Table 2.

The maximum efficiency, *E* (%), of 84% is achieved when the concentration of HIO_4 is 0.15 mmol. This may be due to increase the numbers of aldehyde groups by using HIO_4 (He et al., 2004; Zheng et al., 1996; Lan et al., 2002) lead to more active sites for starch grafting reaction. When the amount of HIO_4 is increased from 0.1 mmol to 0.15 mmol, the *E* (%) was increases by 3%, but the homopolymer was decreased. When the amount of HIO_4 is increased from 0.15 mmol to 0.20 mmol, the *E* (%) was decreases by 2%, the homopolymer was slightly increased, and the solution turns purplish red when the product dissolved in water. This phenomenon indicates that the presence of excess initiator causes some residues in the graft product, 0.15 mmol is enough for the reaction when the starch is ungelatinized. After adding periodic acid, *E* (%) is improved.

3.2.2. Effect of periodic acid on graft copolymerization under gelatinization

The gelatinization temperature (70, 80, 90 and 95 °C) on graft copolymerization was investigated. As a result, higher *G* (%), *E* (%) and *α* (%) could be obtained when gelatinization temperature was at 80 °C. Then the effect of amount of periodic acid on graft copolymerization was studied. First, dried starch and distilled water were mixed and stirred at 80 °C for 30 min under nitrogen atmosphere to obtain a gelatinized starch. The mixture was then cooled down to 65 °C. $KMnO_4$ (0.15 mmol) and HIO_4 (0–0.25 mmol) were added continuously. Then AM monomer was added to the reaction mixture. The effect of amount of periodic acid on *α* (%), *G* (%), and *E* (%) under gelatinization is shown in Table 3.

When HIO_4 (0.11 mmol) is added at 80 °C gelatinization temperature, *G* (%) is increased by 18%, and *E* (%) is increased by 16%. Repeat this experiment; the experimental results were the same, indicating good reproducibility of the experiment. When the amount of $KMnO_4$ was increased to 0.3 mmol, the grafting parameters did not

Table 3
Effect of periodic acid on graft copolymerization under gelatinization[a].

$KMnO_4$ (mmol)	HIO_4 (mmol)	α (%)	G (%)	E (%)
0.15	0	98	72	74
0.15	0.11	99	90	90
0.30	0.11	98	89	92
0.15	0.25	99	90[b]	93[b]

[a] Reaction conditions: starch to AM ratio, 1: 1; pH, 1; gelatinization temperature, 80 °C; gelatinization time, 30 min; graft reaction temperature, 65 °C.
[b] The initiator was excessive; therefore, the product color was deepened.

significantly change, but the product was slightly yellow, indicating an excess of $KMnO_4$. When the amount of HIO_4 was increased to 0.25 mmol, aqueous solution of the graft product turned purplish red. We could speculate that 0.11 mmol of HIO_4 is sufficient while gelatinized, and the excess amount of HIO_4 is not beneficial to the reaction.

3.3. Effect of pre-oxidation condition on graft copolymerization

The effect of pre-oxidation condition on E (%) and viscosity of the product is shown in Table 4. Table 4 shows that E (%) was the largest when the initiation process involved simultaneous addition of $KMnO_4$ and HIO_4 into the starch that is pre-oxidizing for 10 min and then monomers and acid were added; compared with a separate using $KMnO_4$(entry 1) E (%) increased by 8%, the product viscosity also increased (Table 4, entry 5). It explains that HIO_4 increased active sites of starch molecular structures, and the number of branched chains grafted on the starch molecules increased, which increased the G (%) of grafted products and viscosity. The main function of the HIO_4 initiator is to open the starch ring and form two more aldehyde groups. Mn^{4+} which generated during oxidation of the primary hydroxyl groups of glucose units by $KMnO_4$ reacted with aldehyde groups to produce free radicals to initiate graft polymerization. If HIO_4 is first added to perform oxidation for a long time and then $KMnO_4$ is added, the latter would further oxidize two aldehyde groups to two carboxyl groups generated from HIO_4. Carboxyl groups could not react with Mn^{4+} or Mn^{3+} to generate free radicals so that E (%) would reduce. Therefore, dosage and means of adding $KMnO_4$ and HIO_4 should be controlled strictly.

3.4. Characterization of graft copolymer by FTIR

IR spectrum of St-g-PAM has the characteristic absorption peaks representing both starch and carbonyl group of the acylamide. IR

Table 4
Effect of pre-oxidation condition on graft copolymerization[a].

Pre-oxidation condition	Crude product (g)	Homopolymer (%)	E (%)	Viscosity (mPa s)
Adding $KMnO_4$ for 10 min reaction	8.3711	12.5	76	24
First adding HIO_4 for 5 min reaction, then adding $KMnO_4$ for 5 min reaction	8.0305	9.2	82	31
First adding $KMnO_4$ for 3 min reaction, then adding HIO_4 for 7 min reaction	8.5166	9.4	82	31
First adding $KMnO_4$ for 5 min reaction, then adding HIO_4 for 5 min reaction	8.6600	9.7	82	31
Adding $KMnO_4$ and HIO_4 at the same time for 10 min reaction	8.7316	8.6	84	34

[a] Reaction conditions: starch to AM ratio, 1:1; [$KMnO_4$], 0.15 mmol; [HIO_4], 0.11 mmol; pH, 1; graft reaction temperature, 65 °C.

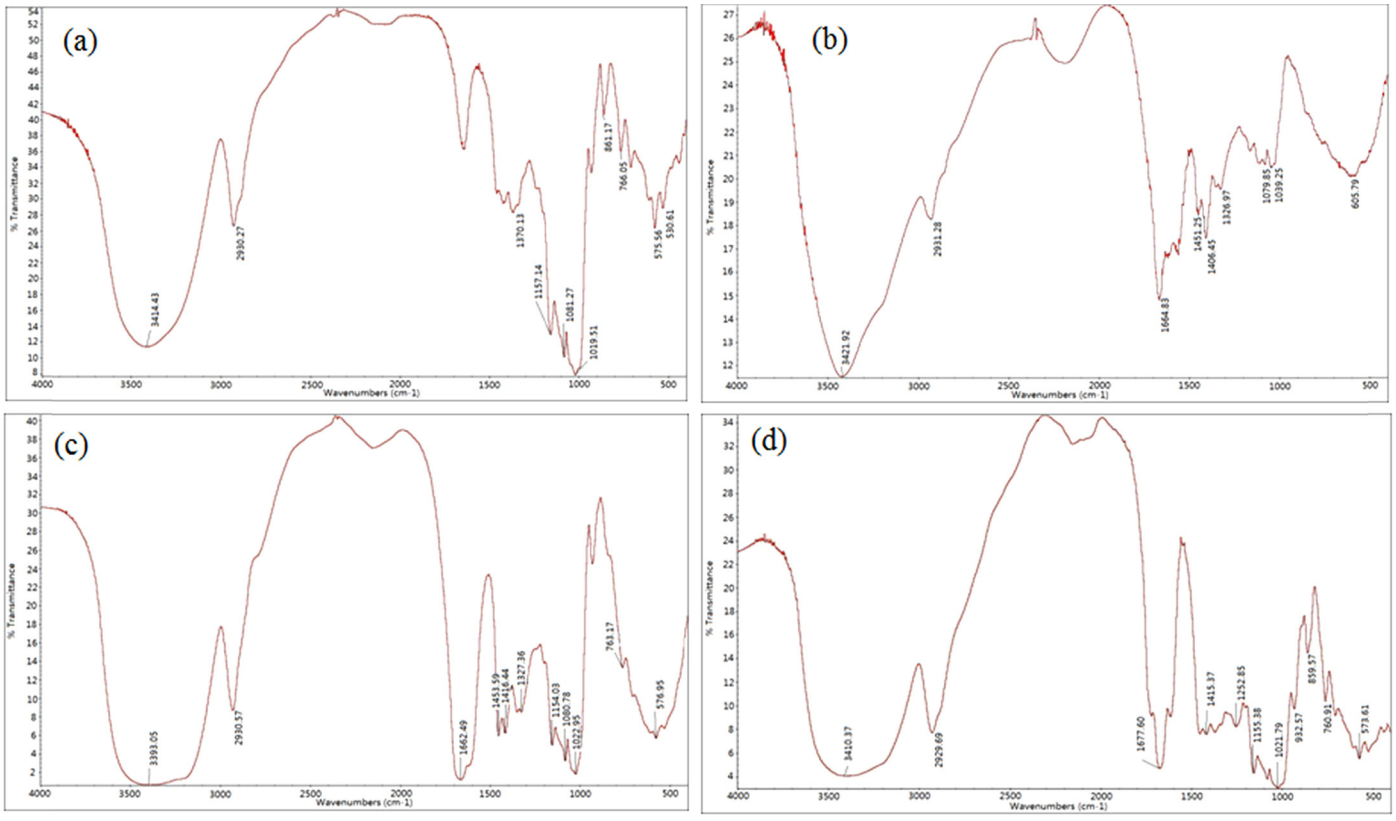

Fig. 1. IR Spectra of (a) corn starch, (b) PAM, (c) Mechanical mixture of starch and PAM, and (d) starch graft PAM.

Table 5
Elemental analysis.

Sample	Element content (%)		
	C%	H%	N%
1[a]	43.82	6.74	8.08
2[b]	43.45	6.75	8.53

[a] St-g-PAM, obtained after initiation with $KMnO_4/H_2SO_4$.
[b] St-g-PAM, obtained after initiation with $KMnO_4/HIO_4/H_2SO_4$.

spectra of corn starch, PAM, mechanical mixture of starch and PAM, and St-g-PAM are represented in Fig. 1.

Grafted starch (Fig. 1d) has the characteristic starch absorption peaks (Fig. 1a) at 573, 760, 859, 1021, and 1081 cm^{-1}, in addition to the characteristic carbonyl peak at 1677 cm^{-1}, which indicates that the graft polymerization of starch and PAM has occurred. The carbonyl peak in PAM (Fig. 1b) is observed at 1664 cm^{-1}, and the same in the mechanical mixture of starch and PAM (Fig. 1c) occurs at 1662 cm^{-1}. However, the carbonyl peak in the IR spectrum of starch graft co-polymer (Fig. 1d) is observed at 1677 cm^{-1}. From the above data, it is clear that the characteristic carbonyl absorption peaks of the mechanical mixture and PAM are close to each other, while the carbonyl peak in the graft polymer is red shifted (by 13 cm^{-1} when compared with the carbonyl peak in PAM). This provides further proof for the successful co-polymerization of starch and AM.

3.5. Characterization of graft copolymer by elemental analysis

Elemental analysis of the obtained graft copolymers (Table 5) reveals that the nitrogen content in the product obtained after initiation with $KMnO_4/HIO_4$ is higher than that in the product obtained after initiation with $KMnO_4$ by 0.45%, which indicates that the amount of AM in St-g-PAM product obtained after initiation with $KMnO_4/HIO_4$ is higher than that obtained after initiation with $KMnO_4$ alone.

3.6. Characterization of graft copolymer by SEM

The SEM photographs of corn starch, oxidized starch, and St-g-PAM obtained after initiation by $KMnO_4$ and $KMnO_4/HIO_4$ are shown in Fig. 2.

The corn starch granules (Fig. 2a) have an irregular shape with a smooth surface and they are disperse, while the graft copolymers (Fig. 2c and d) have lost the original granular structure of starch and form flocculent network structures. There are two reasons for the observed structural modifications. First, at 65 °C, starch begins to swell and absorb water, and the structural integrity of the starch granules is further destroyed by the action of oxidizing agent (Fig. 2b). Second, grafting of PAM onto particulate starch or damaged starch leads to cross linking and formation of complex structures where both PAM and starch are covered with each other. Such remarkable changes in the structure before and after grafting indicate the successful grafting of PAM on starch. The

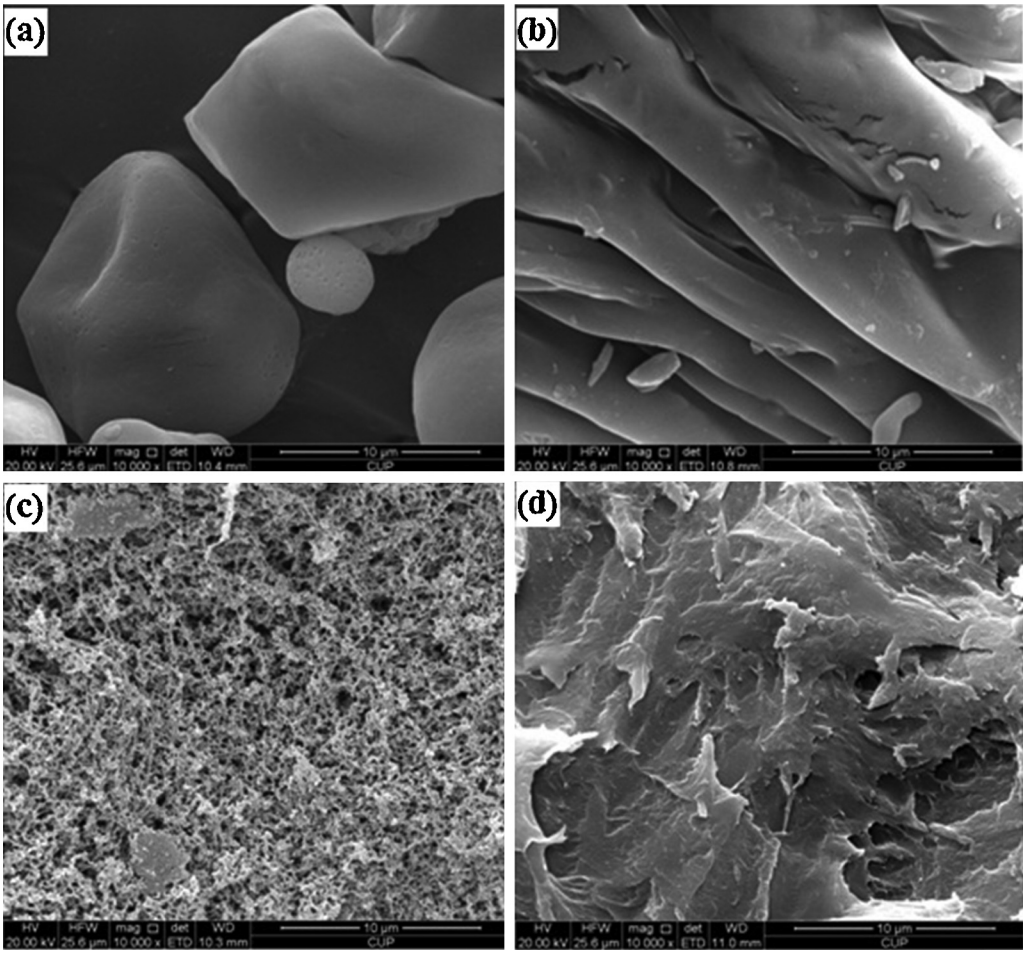

Fig. 2. SEM image of (a) corn starch, (b) oxidized starch, (c) starch graft PAM obtained after using $KMnO_4/H_2SO_4$, and (d) starch graft PAM obtained after using $KMnO_4$ and HIO_4/H_2SO_4.

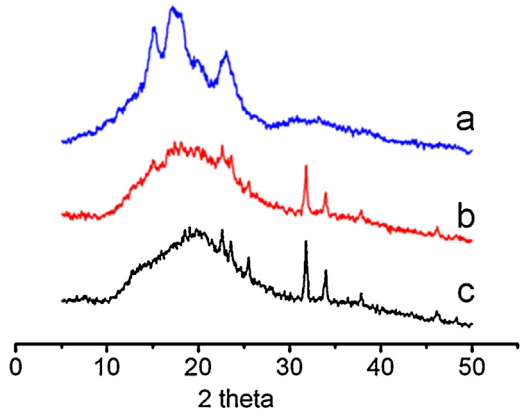

Fig. 3. *X-ray diffraction patterns of corn starch and starch graft PAM.* (a) corn starch (b) ungelatinized starch graft PAM (graft reaction temperature, 65 °C) (c) gelatinized starch graft PAM (gelatinization temperature, 90 °C).

structure of the co-polymer obtained when the co-polymerization is initiated by $KMnO_4/HIO_4$ is stacked closely (Fig. 2d), it is different from that obtained when the co-polymerization is initiated by $KMnO_4$, which indicates a role for HIO_4 in the co-polymerization. From the data of *E* (%) previously calculated, it is likely that HIO_4 opened up rings, thereby increasing the number of active sites.

3.7. Characterization of graft copolymer by XRD

The X-ray diffraction patterns of corn starch, gelatinized starch graft copolymer at 90 °C, and ungelatinized starch graft copolymer at 65 °C are illustrated in Fig. 3.

Fig. 3 shows XRD patterns of native starch (Fig. 3a) exhibiting sharp characteristic diffraction peaks and dispersion characteristic diffraction peaks, which suggested that native starch was semi-crystalline, but characteristic diffraction peaks of starch disappeared in XRD patterns of grafted starch (Fig. 3b and c). This indicated that the grafting reaction and water had changed the starch structure and the crystalline state of aggregation.

3.8. Characterization of graft copolymer by NMR

Grafting of the polyacrylamide onto starch was confirmed from the ^{13}C MAS NMR spectrum in Fig. 4 below. The peaks at 102.1, 81.4, 72.2 and 61.5 ppm were the characteristic signals of starch. The peaks at 179.3 and 41.3 ppm belong to the signals of $CONH_2$ and CH_2 groups in the polyacrylamide. This suggests the successful grafting of polyacrylamide on starch. It is worth noting that the weak signal at 168.9 ppm should be attributed to the presence of COOH group which was generated by excessive oxidation of aldehyde groups. This may explain why the crude product weight is higher than the total weight of corn starch and monomer.

4. Study on the mechanism of an innovative composite initiator of $KMnO_4$, HIO_4/H_2SO_4

On the basis of the experimental results and published research, we speculate the mechanism of initiation by the $KMnO_4/HIO_4$ composite system. First, $KMnO_4$ oxidizes the primary hydroxyl on the unit ring of starch to an aldehyde, while it itself is reduced to MnO_2. Mn^{4+} reacts with the enol form of the aldehyde to generate free radicals, which initiates the graft polymerization. It is noteworthy that Mn^{3+} is generated during the production of free radicals, since Mn^{3+} can also react with another enol to produce free radicals (Wang et al., 1998; Gao, Yu, Wang, Zhang, & Tian, 2000). That is, if there are a sufficient number of aldehydes available, each molecule of $KMnO_4$ can generate two radical sites. Thus, the addition of a small amount of HIO_4 in the $KMnO_4/H_2SO_4$ system can lead to simultaneous generation of three aldehyde groups in the unit ring of starch, one by a $KMnO_4$ molecule and two by each HIO_4 molecule

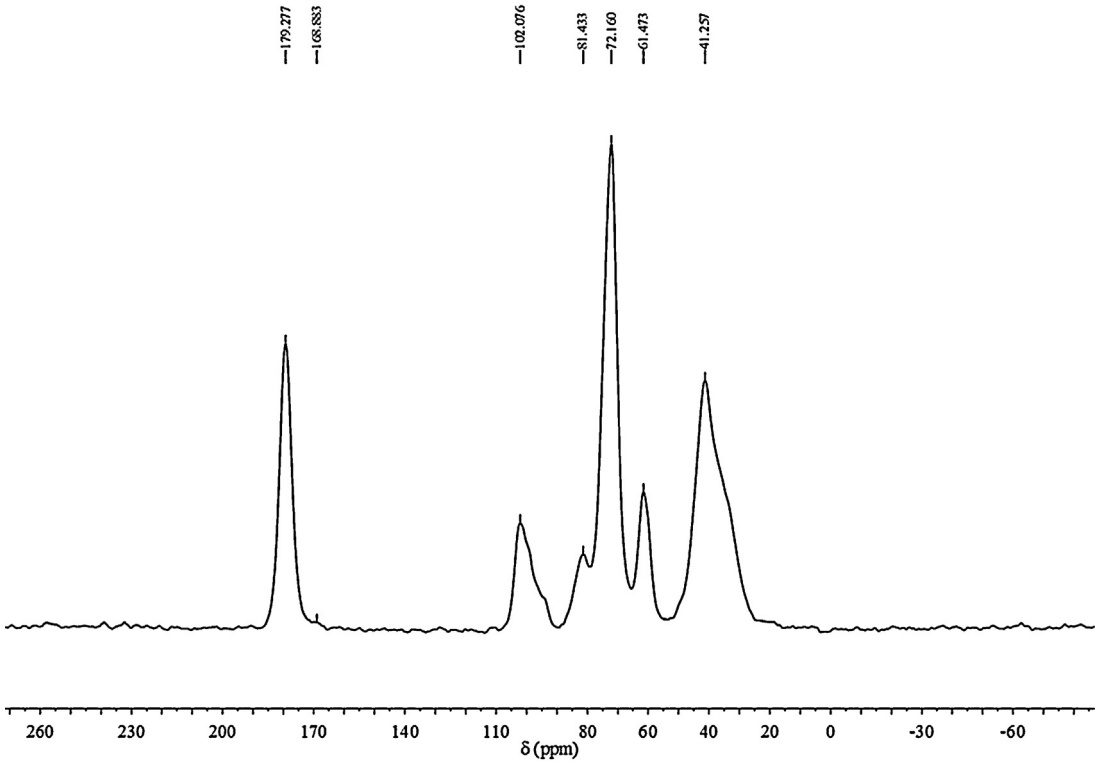

Fig. 4. ^{13}C MAS NMR spectrum of starch graft PAM initiated by $KMnO_4/HIO_4/H_2SO_4$.

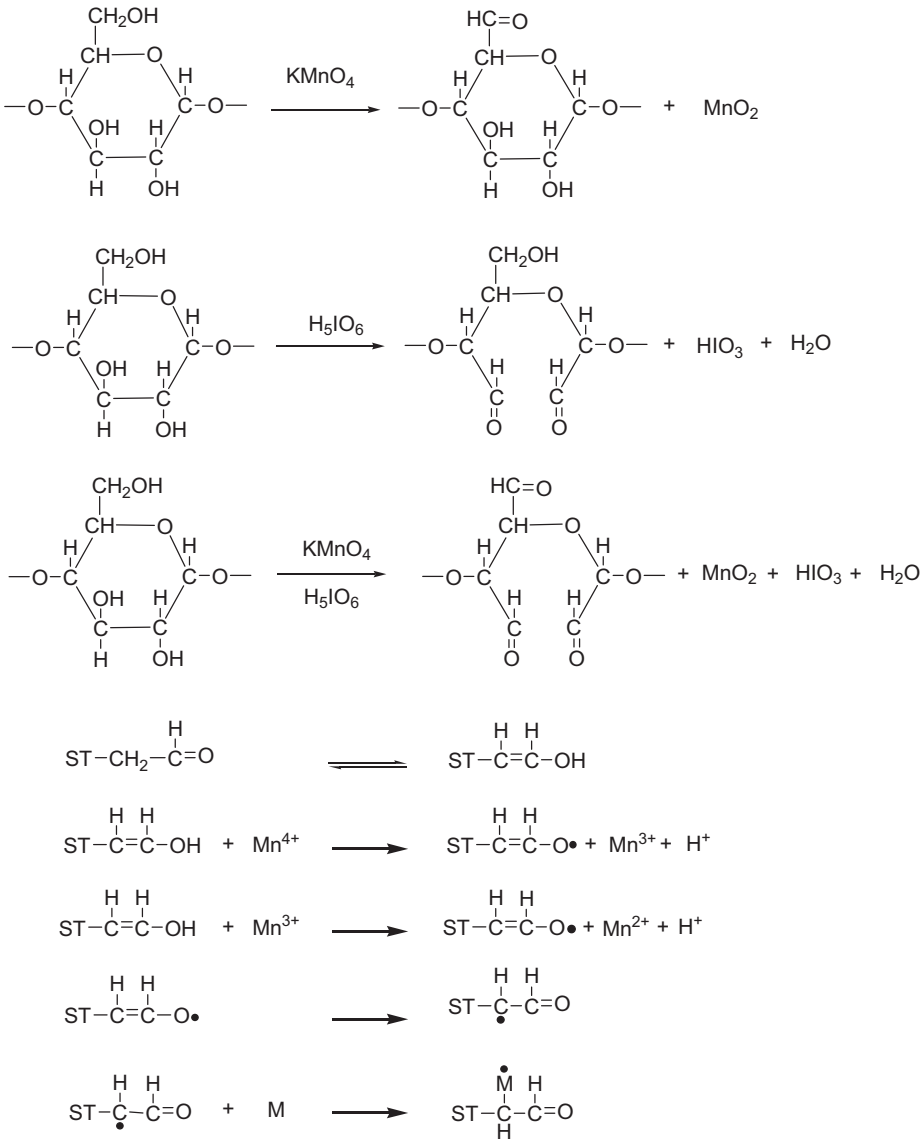

Fig. 5. *Initiation mechanism of composite initiator.* ST represents glucose unit rings in the starch, and M represents the monomer.

(Zhang, Zhu, Zhang, & Lin, 2002). Then, both Mn^{4+} and Mn^{3+} can react with aldehyde groups to generate two free-radical sites that can serve as the origin for the graft (both initiation points and graft points of free radical chain reaction), and the third aldehyde group can also produce free radicals (grafting sites) in the subsequent radical chain reaction. Therefore, addition of HIO_4 increases the number of aldehyde groups in the glucose ring in the starch, which in turn increases the efficiency of manganese ions, and increases the origin sites of free radicals. The grafting efficiency could be improved in theory. The proposed reaction mechanism is shown in Fig. 5.

5. Conclusions

This study describes a process for the generation of a graft starch copolymer where the grafting of the co-polymer is initiated with the use of a new composite initiator system that contains $KMnO_4$ and HIO_4 in the presence of H_2SO_4. Compared with ungelatinizing and using $KMnO_4$ alone, in this system, initiated St-g-PAM *E* (%) increased by 8% and homopolymer content decreased by 3.9%. *G* (%) increased by 18% and *E* (%) improved by 16% upon the application of this system gelatinizing for 30 min at 80 °C. The repeatability of these experiments was good. The results show that the addition of HIO_4 increases the number of active sites in starch, thus improving *G* (%) and *E* (%). Experimental results are consistent with the theoretical speculation. Further experiments show that the sequence and time of HIO_4 addition influence the graft polymerization reaction. The grafted product was characterized by IR, SEM, NMR and XRD, which show that PAM has been successfully grafted onto starch molecules.

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