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Gamma radiation-induced grafting of acrylamide and dimethyl diallyl ammonium chloride onto starch

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ABSTRACT

Corn starch graft copolymers were prepared from acrylamide/dimethyl diallyl ammonium chloride binary monomers (AM/DMDAAC) by a simultaneous radiation grafting method, and were characterized by FTIR and ^{1}H NMR techniques, weight measurement and titration method. The copolymers with high grafting ratio and high grafting efficiency of binary monomers were achieved at absorbed doses of 2 kGy and 3 kGy using a 6:9.8:4.2 (w/w/w) ratio of starch/AM/DMDAAC, but their cationic degrees were low. Grafting ratio, grafting efficiency and cationic degree of the copolymers increased with increasing AM content in comonomer mixtures and then decreased at 3 kGy using a 6:14 ratio of starch:total comonomers, but their cationic degrees generally decreased with increasing AM content. The grafting ratio, the grafting efficiency and the cationic degree of the copolymers increased, but the grafting efficiency of DMDAAC decreased with varying starch/(AM + DMDAAC) ratio from 6:3 to 6:18 at 3 kGy by using a fixed 7:3 ratio of AM:DMDAAC.

1. Introduction

Starch comprises a mixture of two polysaccharides: amylose (a linear polysaccharide) and amylopectin (a branched polysaccharide). Molecules of the former polysaccharide consist of weakly branched polysaccharide chains composed of glucose residues linked by valence bonds, while the latter has a more complicated structure of branched chains. As one of the most abundant substances in nature, starch is not only the primary source of food for the humans, but can also be regarded as renewable resource that may be utilized in many industrial applications. But native starches have limited usage due to its inherent weakness of hydration, swelling and structural organization. In order to enhance viscosity, texture, stability among many desired functional properties desired for many food and industrial applications, starch and their derivatives are modified by chemical, physical and biotechnology means. Starch modification involving the alteration of the physical and chemical characteristics of specific industrial applications, is generally achieved through derivatization such as esterification, etherification, cross linking, acid hydrolysis, enzymatic hydrolysis, heat treatment and grafting of starch (Singh, Nath, & Singh, 2010).

As an important aspect of starch modification, graft copolymerization of starch with a variety of vinyl monomers is initiated either by a chemical free radical initiator (e.g. ceric ammonium nitrate or ammonium persulfate) (Athawale & Lele, 2000; Chen, Park, & Park, 1999) or by high energy radiation (e.g. gamma ray or electron beam) (Kiatkamjornwong, Mongkolsawat, & Sonsuk, 2002; Song, Zhang, Ma, Wang, & Yang, 2007). The chemical free radical initiator is used to generate free radical sites on the polysaccharide backbones, where the monomers are added up to form the graft chain. This method of synthesis has low reproducibility and is not very suitable for commercial scale synthesis. A better method of graft copolymer synthesis is by using high energy radiation as the free radical generator. Radiation-induced grafting is of high efficiency and does not cause any further contamination associated with chemical initiators (Khalek & Mahmoud, 2011). On the other hand, there are four methods of grafting of starch: dry, semi-dry and wet processes. Dry and semi-dry processes are more efficient and more ecological than wet process. But wet process is more mature than others, including the more heterogeneous reactions of granular starch in a slurry and the more homogeneous reactions of gelatinized starch in a paste, which is referred to as the slurry process and the paste process. Reactive extrusion is an efficient approach for starch graft copolymers because it is easy, inexpensive and has a short processing time. Although

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Abbreviations: AM, acrylamide; DMDAAC, dimethyl diallyl ammonium chloride; St-*g*-p(AM-*co*-DMDAAC), starch-graft-poly(acrylamide-*co*-dimethyl diallyl ammonium chloride).

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reactive extrusion has numerous advantages one of the limitations is degradation of the polymer under the high temperatures and mechanical stresses encountered (Kalambur & Rizvi, 2006; Moad, 2011; Nakason, Wohmang, Kaesaman, & Kiatkamjornwong, 2010; Xie, Yu, Liu, & Chen, 2006).

Cationic starches, which are widely used in many fields (Haack, Heinze, Oelmeyer, & Kulicke, 2002; Khalil & Aly, 2001), can be obtained through the grafting reaction of starch with an ethylenically unsaturated monomer having cationic groups initiated either by gamma irradiation (Carr, 1994; Fanta, Burr, Doane, & Russell, 1974; Jones & Elmquist, 1973; Jones & Jordan, 1971; Peoria, 1984) or by a chemical free radical initiator (Liu, Li, & Xu, 2011; Lu, Lin, & Yao, 2004). In general, cationic groups may be amino, immonium, ammonium, sulphonium or phosphonium. Compared with amino and immonium groups, quaternary ammonium group is preferred because the final product does not require any further cationization.

Graft copolymerization of starch with acrylamide (AM) and dimethyl diallyl ammonium chloride (DMDAAC) was reported to be carried out using a complex initiation system (Liu et al., 2011; Lu et al., 2004). And a series of cationic starch graft copolymers have been developed by gamma-ray irradiation of starch and quaternary ammonium salt monomers (Fanta et al., 1974; Jones & Elmquist, 1973; Jones & Jordan, 1971; Peoria, 1984). But the graft copolymerization of starch with AM and DMDAAC initiated by gamma irradiation has not been previously reported. Furthermore, Tanaka had investigated the radical copolymerization of DMDAAC (M_1) with acrylamide (M_2) at pH 6.1 in aqueous solutions, and the reactivity ratios were determined to be 0.58 and 6.7 for the pair of monomers (Tanaka, 1986), which implies that DMDAAC is prone to copolymerization with AM instead of homopolymerization due to the electrostatic repulsion between the charged monomer and the charged radical chain end. Therefore, the presence of AM in the graft copolymerization of starch with DMDAAC is expected to facilitate graft copolymerization of DMDAAC onto starch.

Based on the existing literature, the present study has been conducted to synthesize cationic starch by graft copolymerization of starch, AM and DMDAAC by means of simultaneous gamma irradiation. The effects of the reaction parameters, such as the total absorbed dose, mass ratio of AM to DMDAAC, mass ratio of starch to comonomers, and monomer concentration on the grafting parameters were systematically investigated.

2. Experimental

2.1. Materials

Food grade corn starch powder was supplied from Henan Yongchang Starch Sugar Co., Ltd. Dimethyl diallyl ammonium chloride (DMDAAC, AR grade) was purchased from Shandong Luyue Chemical Co., Ltd. Acrylamide (AM, AR grade) was obtained from Tianjin No. 3 Chemical Reagent Factory. All other chemicals were A.R. grade. Double distilled water was used for preparation and measurements.

2.2. Radiation induced graft polymerization

A mixture of corn starch powder and distilled water was continuously stirred using a mechanical stirrer under nitrogen atmosphere in water bath at 85 °C for 30 min. The obtained gelatinized corn starch was mixed with AM and DMDAAC, and continuously stirred to form a homogenous mixture under nitrogen atmosphere. Thereafter, the homogenous mixture was transferred into a wide-mouth, screw-cap glass bottle and repressured with nitrogen four times to remove dissolved oxygen. The bottle was tightly closed with a cap, irradiated with cobalt 60 to a required absorbed dose at 40 Gy/min dose rate, and allowed to stand at ambient temperature for 2 h.

2.3. Determination of grafting ratio and grafting efficiency of total monomers

The rubbery product obtained was broken up, washed with ethanol, vacuum-dried at 60 °C and ground into fine powder. The powder was extracted continuously for 18 h in a Soxhlet extractor with a mixture of acetone and glacial acetic acid (1:1, v/v), and thus ungrafted poly(AM-*co*-DMDAAC) and unreacted monomers were removed from the powder. The graft copolymer St-*g*-p(AM-*co*-DMDAAC) after solvent extraction was dried in a vacuum oven at 60 °C to a constant weight.

Grafting performance in terms of percentage grafting ratio and grafting efficiency of binary monomers was determined by weight measurement. The percentage grafting ratio was calculated as shown in Eq. (1).

$$\text{Grafting ratio} = \frac{\text{Weight of starch grafted copolymer}}{\text{Weight of starch}} \times 100\% \qquad (1)$$

The percentage grafting efficiency of total monomers was calculated by Eq. (2).

$$\text{Grafting efficiency of total monomers} = \frac{\text{Weight of starch grafted copolymer} - \text{Weight of starch}}{\text{Weight of AM} + \text{Weight of DMDAAC}} \times 100\%. \qquad (2)$$

2.4. Determination of cationic degree and grafting efficiency of DMDAAC

Cationic degree of St-*g*-p(AM-*co*-DMDAAC) copolymer was determined by titration (Mohr's method) (Block & Waters, 1967), which depended upon the amount of DMDAAC units incorporated into the copolymer. The starch graft copolymer was weighed into 250 ml Erlenmeyer flask and dissolved in 100 ml of distilled water, and then the pH value of the solution was adjusted between 6.5 and 7.2. Potassium chromate served as the end point indicator in the titration of chloride ions with a silver nitrate standard solution, and the color changed from yellow to brick-red which signaled the end point of this titration. Cationic degree used in m mol/g was calculated by Eq. (3).

$$\text{Cationic degree} = \frac{\text{Molarity of AgNO}_3 \times (V_{\text{AgNO}_3} - V^0_{\text{AgNO}_3})}{\text{Weight of starch grafted copolymer}} \qquad (3)$$

where Molarity of AgNO_3 is used in mol/l or m mol/ml, V_{AgNO_3} is the volume of the silver nitrate standard solution consumed during titration used in ml, $V^0_{\text{AgNO}_3}$ is the volume of the silver nitrate standard solution consumed during blank titration used in ml.

Based on the value of cationic degree, corresponding grafting efficiency of DMDAAC alone was calculated by Eq. (4).

$$\text{Grafting efficiency of DMDAAC alone} = \frac{M_{\text{DMDAAC}} \times \text{Cationic degree}}{1000} \times \frac{\text{Total weight of starch and monomers}}{\text{Weight of DMDAAC}} \times 100\% \qquad (4)$$

where M_{DMDAAC} is molecular weight of DMDAAC. Grafting efficiency of DMDAAC with excluding AM implied the ratio of the weight of grafted DMDAAC monomer to the total weight of initial DMDAAC monomer.

2.5. FTIR study

For IR analysis, the St-*g*-p(AM-*co*-DMDAAC) graft copolymer was prepared in the form of potassium bromide pellet containing 10–15 mg of the graft copolymer and 200 mg of potassium bromide, which was mixed and ground in an agate mortar. The FTIR spectrum was recorded from the KBr pellet in the range 4000–400 cm^{-1} on a Bio-Rad FTS 135 spectrometer.

2.6. NMR study

Proton nuclear magnetic resonance spectra were recorded in deuterium oxide (D_2O) on a Bruker Avance 300 MHz, Germany. Chemical shifts were recorded as Δ values in parts per million (ppm) and referenced to the solvent used (i.e. D_2O).

3. Results and discussion

3.1. Characterization of the functional groups of the copolymers by FTIR

The FTIR scan, in Fig. 1, shows the characteristic absorption bands of AM at 1623 cm^{-1} and 1655 cm^{-1} due to —NH—. This FTIR of St-*g*-p(AM-*co*-DMDAAC) proves the presence of AM.

To confirm that St-*g*-p(AM-*co*-DMDAAC) polymers contained DMDAAC, proton (^1H) nuclear magnetic resonance spectra of the sample were recorded in deuterium (D_2O). Although ^1H NMR of St-*g*-p(AM-*co*-DMDAAC) polymers is complicated due to the cis and trans configurations of the DMDAAC groups within the DMDAAC polymer chains (Kriz, Dybal, & Kurkova, 2002; McLean, Agarwal, Stack, Horne, & Richardson, 2011), the chemical shifts in 3.444–2.459 ppm prove the presence of the DMDAAC polymer chains in the St-*g*-p(AM-*co*-DMDAAC) polymers as shown in Fig. 2. The reaction mechanism of graft copolymerization of AM and DMDAAC onto the backbone of corn starch is proposed in Scheme 1.

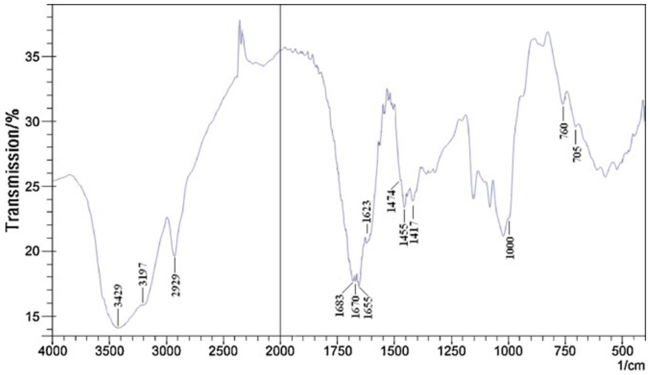


Fig. 1. FTIR spectrum of St-*g*-p(AM-*co*-DMDAAC) prepared using a 6:5.8:8.4 (w/w/w) ratio of starch:AM:DADMAC in 60 ml water at absorbed dose of 3 kGy.

3.2. Effect of absorbed dose on graft copolymerization

At a fixed starch/AM/DMDAAC ratio of 6:9.8:4.2 g, gamma irradiation induced graft copolymerization of AM/DMDAAC binary monomers onto starch was run in 60 ml water at a dose rate of 40 Gy/min. The effects of absorbed dose on the main characteristics of the copolymers are given in Figs. 3 and 4. Both of grafting ratio and grafting efficiency of AM/DMDAAC binary monomers increased initially with increasing absorbed dose up to 2 kGy and then decreased with increasing dose. However, with further increase in absorbed dose up to 5 kGy, grafting ratio and grafting efficiency of total monomers increased to 72% and 74%, respectively.

The initial increase in absorbed dose enhanced the formation of increased amount of the radicals on the starch backbones, which resulted in high grafting ratio and efficiency. And the decrease in grafting ratio thereafter was attributable to starch degradation and enhanced solubility of highly grafted fragments in the precipitating medium (Hofreiter, 1977). Whereas remarkably high grafting ratio and grafting efficiency at 5 kGy should be attributed to the

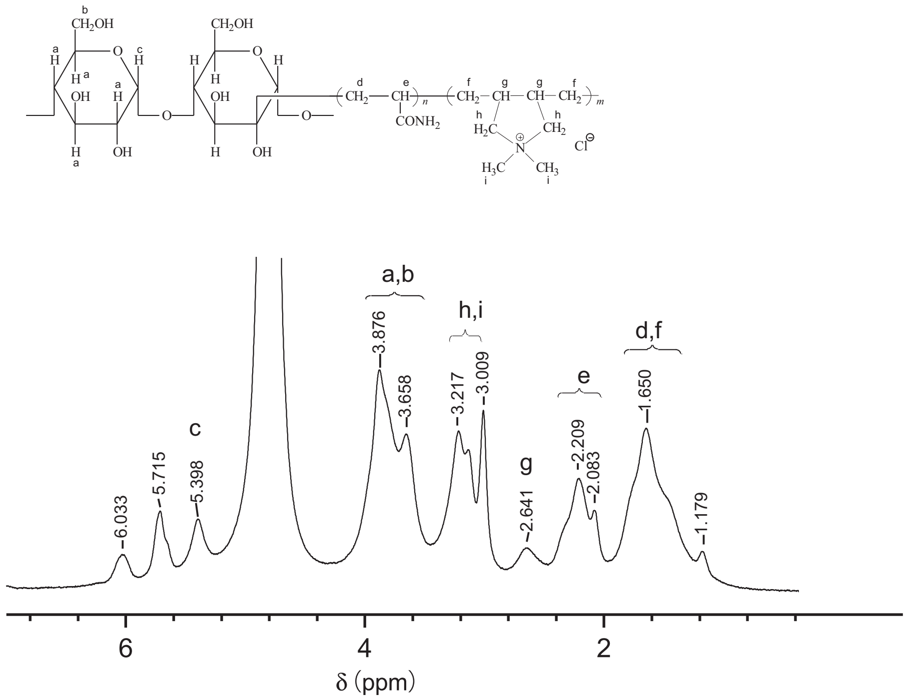
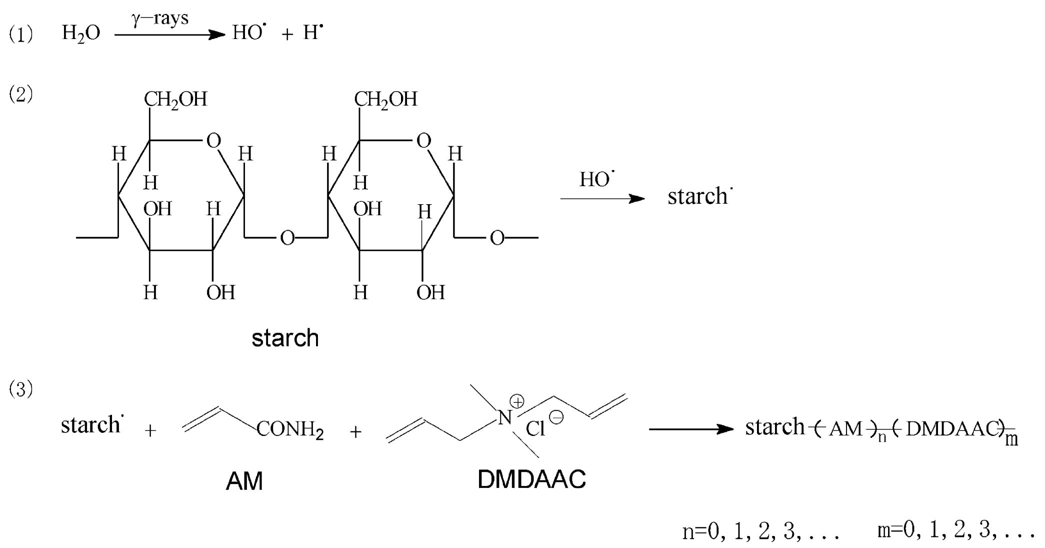


Fig. 2. ^1H NMR spectrum of St-*g*-p(AM-*co*-DMDAAC) prepared using a 6:5.8:8.4 (w/w/w) ratio of starch:AM:DADMAC in 60 ml water at absorbed dose of 3 kGy.



Scheme 1. Reaction mechanism of graft copolymerization of AM and DMDAAC onto corn starch initiated by gamma radiation.

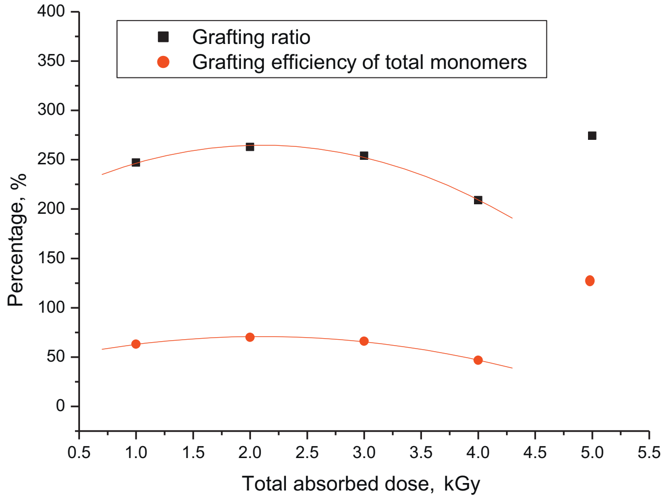


Fig. 3. Influence of absorbed dose on grafting ratio and grafting efficiency of total monomers at starch/AM/DMDAAC/water ratio of 6:9.8:4.2 g:60 ml.

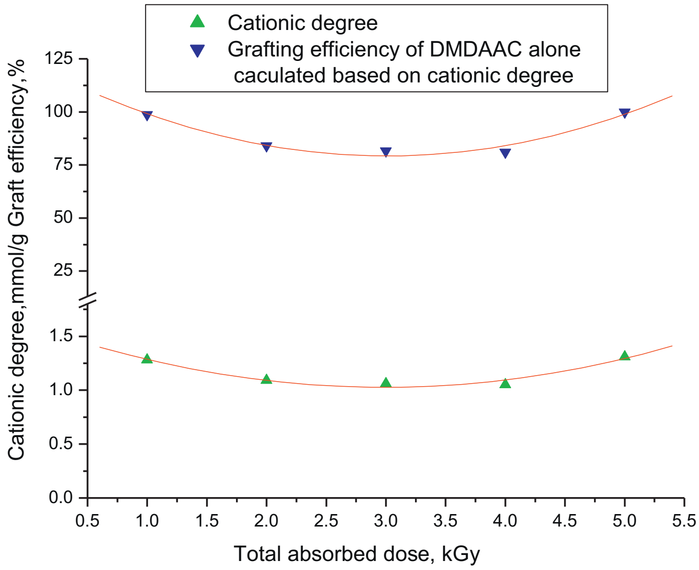


Fig. 4. Influence of absorbed dose on cationic degree and grafting efficiency of DMDAAC at starch/AM/DMDAAC/water ratio of 6:9.8:4.2 g:60 ml.

formation of crosslinking network in the starch graft copolymer (El-Din, Alla, & El-Naggar, 2007; Mishra, Bajpai, Katare, & Bajpai, 2007; Pande & Sharma, 2002), which was resulted from radiation crosslinking of polyacrylamide.

Cationic degree and grafting efficiency of DMDAAC, contrary to that of grafting ratio and grafting efficiency of AM/DMDAAC binary monomers, decreased initially with increasing absorbed dose up to 3 kGy, and then increased. Cationic degree and grafting efficiency of DMDAAC at lower doses (1 kGy and 2 kGy) were higher than those at higher dose (3 kGy), perhaps because the grafting of DMDAAC was almost completed at lower absorbed dose.

Grafting efficiency of total monomers in the investigated conditions was between 46% and 71%, which is at the low end of the results of Lu et al. (2004) (i.e. 50–86%) where St-g-p(AM-*co*-DMDAAC) was synthesized by using a complex initiation system of CS-KPS. However, grafting efficiency of DMDAAC was more than 80%, especially 100% at 5 kGy. Cationic degree had an average value of 1.12 m mol/g in a dose range of 1–5 kGy. Comparatively, the cationic degree (DC) of the starch-g-p(AM-*co*-DMDAAC) of Lu et al. (2004) had DC from 22% to 32% (i.e. from 1.36 m mol/g to 1.98 m mol/g).

3.3. *Effect of AM/DMDAAC weight ratio on graft copolymerization*

At a ratio of starch/binary monomers 6:14 (w/w) in 60 ml water, where the total weight amount of AM and DMDAAC was constant but the weight ratio of AM:DMDAAC was varied, a series of starch graft polymerization were run at absorbed dose of 3 kGy. The effects of the weight ratio of AM:DMDAAC on grafting ratio and grafting efficiency of binary monomers are represented in Fig. 5. Grafting ratio and grafting efficiency of binary monomers generally increased with increasing AM content in comonomer mixtures as expected (Liu et al., 2011; Wu & Zhang, 2006). DMDAAC was less sensitive toward the graft copolymerization process compared with AM, and thus the higher grafting levels at high AM/DMDAAC ratio were partly attributable to the increase of AM content in comonomer mixtures (Athawale & Rathi, 1997; Gao, Tian, & Zhang, 1996; Gao, Yu, Wang, Chang, & Tian, 1998; Huber & Heineman, 1988; Li, Xu, Pen, & Wang, 2008; Liu et al., 2011; Taghizadeh & Khosravy, 2003).

Similar to those of grafting ratio and grafting efficiency of binary monomers, grafting efficiency of DMDAAC increased with the increase of AM content in comonomer mixtures and slightly

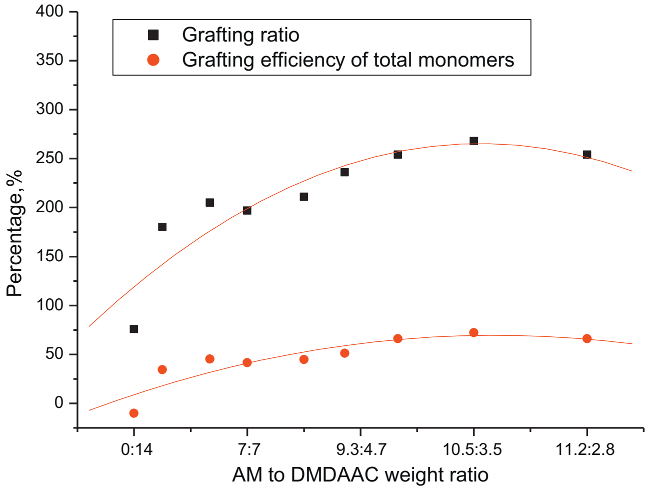


Fig. 5. Dependence of grafting ratio and grafting efficiency of total monomers on AM/DMDAAC weight ratio.

decreased thereafter (Fig. 6). Comparatively, cationic degree gradually decreased with increasing AM/DMDAAC feed ratio (Fig. 6), which was attributed to the decrease of cationic monomer (i.e. DMDAAC) content in comonomer mixtures.

Interestingly, the value of cationic degree increased uncommonly from 0.89 m mol/ml to 1.50 m mol/ml as AM/DMDAAC ratio was raised from 0:14 to 2.8:11.2, which implied that the presence of AM remarkably facilitated grafting of DMDAAC onto starch.

3.4. *Effect of starch/(AM + DMDAAC) weight ratio on graft copolymerization*

Starch graft copolymers were prepared by gamma irradiation up to 3 kGy in 60 ml water at a constant ratio of AM/DMDAAC 7:3, whereas the combined weight of AM and DMDAAC (i.e. AM + DMDAAC) varied and thus starch/(AM + DMDAAC) ratio varied. The influence of starch/(AM + DMDAAC) weight ratio on graft copolymerization is presented in Figs. 7 and 8.

By varying starch/(AM + DMDAAC) ratio from 6:3 g to 6:18 g, grafting ratio increased almost linearly from 90% to 367%, and grafting efficiency of total comonomers increased from 20.3% to 89.0%, respectively.

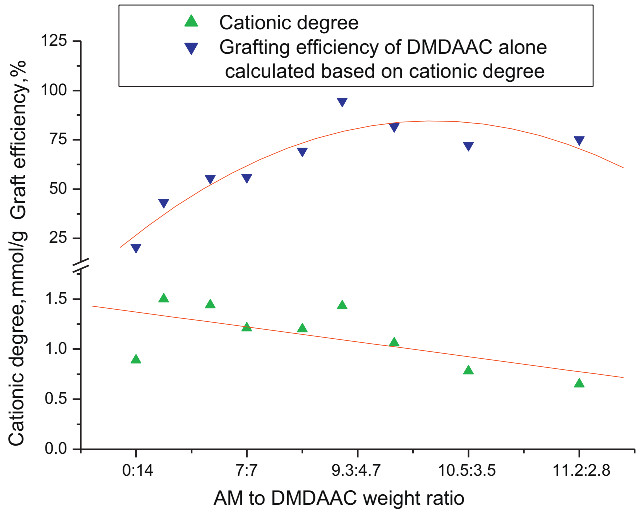


Fig. 6. Dependence of cationic degree and grafting efficiency of DMDAAC on AM/DMDAAC weight ratio.

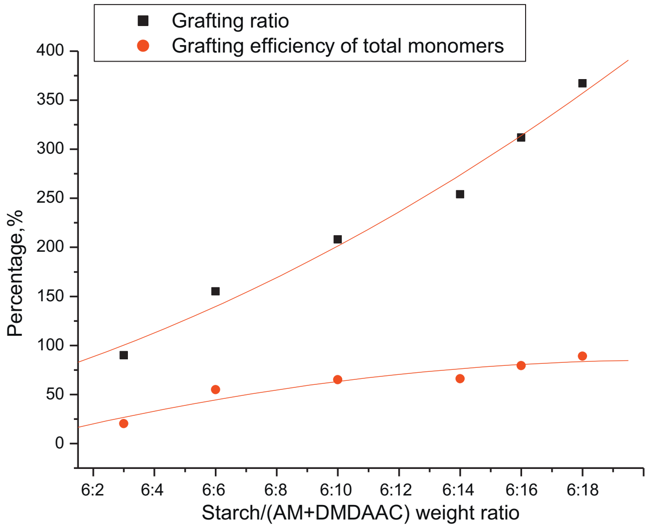


Fig. 7. Dependence of grafting ratio and grafting efficiency of total monomers on starch/(AM + DMDAAC) weight ratio.

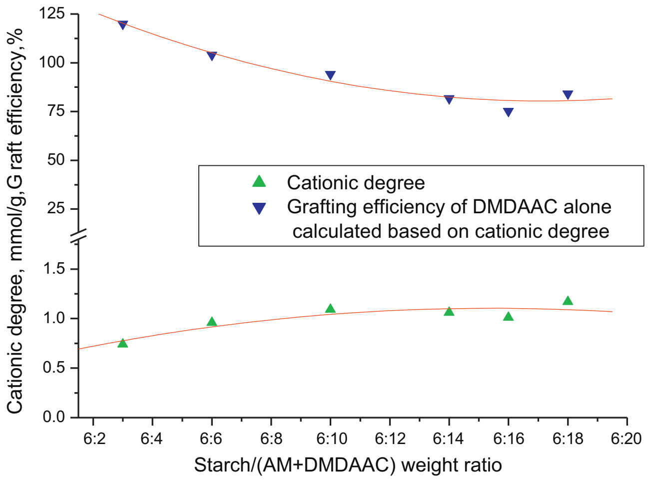


Fig. 8. Dependence of cationic degree and grafting efficiency of DMDAAC on starch/(AM + DMDAAC) weight ratio.

Cationic degree increased from 0.74 m mol/g to 1.17 m mol/g with increasing starch/(AM + DMDAAC) weight ratio from 6:3 g to 6:18 g (Fig. 8), which was similar to that for grafting efficiency of binary monomers in Fig. 7. Contrary to those of other three parameters which increased with starch/(AM + DMDAAC) weight ratio, grafting efficiency of DMDAAC decreased (Fig. 8). This might reasonably be caused by electrostatic repulsion between ungrafted cationic monomer and initially grafted cationic monomer (Fanta, Burr, Doane, & Russell, 1972).

4. Conclusions

The grafting of starch with AM/DMDAAC binary monomer mixtures was achieved through gamma irradiation for the production of cationic starch. FTIR and ^{1}H NMR techniques confirmed the formation of St-*g*-p(AM-*co*-DMDAAC) copolymers. The copolymers with high grafting ratio and high grafting efficiency of binary monomers were obtained at absorbed doses of 2 kGy and 3 kGy using a 6:9.8:4.2 (w/w/w) ratio of starch:AM:DMDAAC, but the copolymers with high cationic degree were obtained at absorbed doses of 1 kGy and 4 kGy. Not only the grafting ratio of binary monomers but also that of DMDAAC alone increased and then decreased with increasing AM content in binary monomer mixtures at absorbed dose of 3 kGy using a 6:14 (w/w) ratio of starch:binary monomer mixture. The grafting ratio of binary monomers and the cationic degree of the copolymers increased, but the grafting efficiency of DMDAAC alone decreased, with increasing the content of binary monomer mixture from 6:3 to 6:18 at absorbed dose of 3 kGy by using a fixed 7:3 (w/w) ratio of AM:DMDAAC.

Conflict of interest

The authors have declared no conflict of interest.

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References

Athawale, V. D., & Lele, V. (2000). Thermal studies on granular maize starch and its graft copolymers with vinyl monomers. *Starch/Stärke*, *52*(6–7), 205–213.

Athawale, V. D., & Rathi, S. C. (1997). Role and relevance of polarity and solubility of vinyl monomers in graft polymerization onto starch. *Reactive and Functional Polymers*, *34*, 11–17.

Block, J., & Waters, O. S. (1967). Interference of the ammonium ion in Mohr's method for the determination of chloride. *Talanta*, *14*(9), 1130–1131.

Carr, M. E. (1994). Preparation of cationic starch containing quaternary ammonium substituents by reactive twin-screw extrusion processing. *Journal of Applied Polymer Science*, *54*, 1855–1861.

Chen, J., Park, H., & Park, K. (1999). Synthesis of superporous hydrogels: Hydrogels with fast swelling and superabsorbent properties. *Journal of Biomedical Materials Research: Part A*, *44*, 53–62.

El-Din, H. M. N., Alla, S. G. A., & El-Naggar, A. W. M. (2007). Radiation synthesis and characterization of hydrogels composed of poly(vinyl alcohol) and acrylamide mixtures. *Journal of Macromolecular Science: Chemistry*, *44*, 47–54.

Fanta, G. F., Burr, R. C., Doane, W. M., & Russell, C. R. (1972). Graft copolymers of starch with mixtures of acrylamide and the nitric acid salt of dimethylaminoethyl methacrylate. *Journal of Applied Polymer Science*, *16*, 2835–2845.

Fanta, G. F., Burr, R. C., Doane, W. M., & Russell, C. R. (1974). Graft copolymers by simultaneous 60Co-irradiation of starch, acrylamide, and N,N,N-trimethylaminoethyl methacrylate methyl sulfate. *Journal of Applied Polymer Science*, *18*, 2205–2209.

Gao, J., Tian, R., & Zhang, L. (1996). Graft copolymerization of vinyl monomers onto starch initiated by transition metal–thiourea redox systems. *Chinese Journal of Polymer Science*, *14*, 163–171.

Gao, J., Yu, J., Wang, W., Chang, L., & Tian, R. (1998). Comparison of transition metals in the graft copolymerization of vinyl monomers onto starch. *Journal of Macromolecular Science Pure and Applied Chemistry*, *35*, 483–494.

Haack, V., Heinze, T., Oelmeyer, G., & Kulicke, W.-M. (2002). Starch derivatives of high degree of functionalization, 8. Synthesis and flocculation behavior of cationic starch polyelectrolytes. *Macromolecular Materials and Engineering*, *287*, 495–502.

Hofreiter, B. T. (1977). Amylose graft polymers made by 60Co gamma-irradiation. *Journal of Applied Polymer Science*, *21*, 761–772.

Huber, E. W., & Heineman, W. R. (1988). The polymerization of dimethyldiallylammonium chloride by gamma irradiation as followed by ^{1}H NMR. *Journal of Polymer Science Part C: Polymer Letters*, *26*, 333–339.

Jones, D. A., & Elmquist, L. F. (1973). Starch graft polymers. III. Preparation of graft polymers containing acrylamide, acrylic acid and β-methacryloyloxyethyltrimethyl ammonium monomethyl sulfate and evaluation as flocculants for Bauxite ore red mud suspensions. *Starch/Stärke*, *25*, 83–89.

Jones, D. A., & Jordan, W. A. (1971). Starch graft polymers. I. Graft co- and terpolymers of starch with 2-hydroxy-3-methacryloyloxypropyl-trimethylammonium chloride and acrylamide: Preparation and evaluation as silica depressants. *Journal of Applied Polymer Science*, *15*, 2461–2469.

Kalambur, S., & Rizvi, S. S. H. (2006). An overview of starch-based plastic blends from reactive extrusion. *Journal of Plastic Film and Sheeting*, *22*, 39–58.

Khalek, M. A. A., & Mahmoud, G. A. (2011). Flocculation studies of fine coal using acrylamide and acrylic acid graft copolymer by gamma irradiation. *Australian Journal of Basic and Applied Sciences*, *5*, 271–278.

Khalil, M. I., & Aly, A. A. (2001). Preparation and evaluation of some cationic starch derivatives as flocculants. *Starch/Stärke*, *53*, 84–89.

Kiatkamjornwong, S., Mongkolsawat, K., & Sonsuk, M. (2002). Synthesis and property characterization of cassava starch grafted poly[acrylamide-co-(maleic acid)] superabsorbent via γ-irradiation. *Polymer*, *43*, 3915–3924.

Kriz, J., Dybal, J., & Kurkova, D. (2002). Cooperative counterion–polyion interactions in polyelectrolyte chain dynamics: NMR and quantum-chemical study of locally collapsed state in dilute poly(N-diallyldimethylammonium chloride) in NaCl/D_2O solutions. *Journal of Physical Chemistry A*, *106*, 7971–7981.

Li, X., Xu, S., Pen, Y., & Wang, J. (2008). The swelling behaviors and network parameters of cationic starch-g-acrylic acid/poly(dimethyldiallylammonium chloride) semi-interpenetrating polymer networks hydrogels. *Journal of Applied Polymer Science*, *110*, 1828–1836.

Liu, Q., Li, J., & Xu, W. (2011). Preparation and application of starch-acrylamide-diallyl dimethyl ammonium chloride graft copolymer. *Materials Science Forum*, *675–677*, 403–406.

Lu, S., Lin, S., & Yao, K. (2004). Study on the synthesis and application of starch-graft-poly(AM-co-DMDAAC) by using a complex Initiation system of CS-KPS. *Starch/Stärke*, *56*, 138–143.

McLean, D., Agarwal, V., Stack, K., Horne, J., & Richardson, D. (2011). Synthesis of guar gum-graft-poly(acrylamide-co-dimethyl diallyl ammonium chloride) and its application in the pulp and paper industry. *BioResources*, *6*, 4168–4180.

Mishra, S., Bajpai, R., Katare, R., & Bajpai, A. K. (2007). Radiation induced crosslinking effect on semi-interpenetrating polymer networks of poly(vinyl alcohol). *Express Polymer Letters*, *1*, 407–415.

Moad, C. (2011). Chemical modification of starch by reactive extrusion. *Progress in Polymer Science*, *36*, 218–237.

Nakason, C., Wohmang, T., Kaesaman, A., & Kiatkamjornwong, S. (2010). Preparation of cassava starch-graft-polyacrylamide superabsorbents and associated composites by reactive blending. *Carbohydrate Polymers*, *81*, 348–357.

Pande, C. S., & Sharma, A. (2002). Functionalization of crosslinked polyacrylamide through γ-radiation-induced grafting of 4-vinylpyridine. *Journal of Applied Polymer Science*, *84*, 2613–2620.

Peoria, M. O. W. (1984). Stabilization of soil particles to water effect of cations. *Starch/Stärke*, *36*, 356–358.

Singh, A. V., Nath, L. K., & Singh, A. (2010). Pharmaceutical, food and non-food applications of modified starches: A critical review. *Electronic Journal of Environmental, Agricultural and Food Chemistry*, *9*, 1214–1221.

Song, H., Zhang, S. F., Ma, X. C., Wang, D. Z., & Yang, J. Z. (2007). Synthesis and application of starch-graft-poly(AM-co-AMPS) by using a complex initiation system. *Carbohydrate Polymers*, *69*, 189–195.

Taghizadeh, M. T., & Khosravy, M. (2003). Kinetics and mechanism of graft copolymerization of vinyl monomers (acrylamide, acrylic acid, and methacrylate) onto starch by potassium dichromate as redox initiator. *Iranian Polymer Journal*, *12*, 497–505.

Tanaka, H. (1986). Copolymerization of cationic monomers with acrylamide in an aqueous solution. *Journal of Polymer Science Part A: Polymer Chemistry*, *24*, 29–36.

Wu, F., & Zhang, X. (2006). Synthesis and characterization of copolymer of dimethyldiallylammoniun chloride and acrylamide. *Advances in Materials Research*, *11–12*, 753–756.

Xie, F., Yu, L., Liu, H., & Chen, L. (2006). Starch modification using reactive extrusion. *Starch/Stärke*, *58*, 131–139.