

Ammonium Persulfate-initiated Graft Copolymerization of Methacrylamide onto Chitosan: Synthesis, Characterization and Optimization

(Cangkukan Kopempolimeran Metakrilamida ke Kitosan oleh Ammonium Persulfat: Sintesis, Pencirian dan Pengoptimuman)

ZETTY AZALEA SUTIRMAN, MOHD MARSIN SANAGI*, AHMEDY ABU NAIM, KHAIRIL JUHANNI ABD KARIM & WAN AINI WAN IBRAHIM

ABSTRACT

Ammonium persulfate (APS)-initiated grafting of methacrylamide (MAM) onto chitosan was successfully prepared for the first time by free radical mechanism. Both chitosan and chitosan-graft-poly(methacrylamide) (chitosan-g-PMAM) were characterized using Fourier transform infrared spectroscopy (FTIR), solid state ¹³C NMR, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). Important factors affecting graft copolymerization such as reaction time, temperature and concentrations of APS, MAM and chitosan were investigated and optimized to obtain maximum grafting parameters. The optimum values for grafting percentage and yield of graft copolymerization were achieved under the following conditions: chitosan (1 g), MAM (4 g), APS (0.6 g), time reaction (4 h) and temperature (70°C).

Keywords: Ammonium persulfate; chitosan; free radical; graft copolymerization; methacrylamide

ABSTRAK

Cangkukan metakrilamida (MAM) kepada kitosan dimulakan oleh ammonium persulfat (APS) telah berjaya disediakan buat kali pertama melalui mekanisme radikal bebas. Kedua-dua kitosan dan kitosan-cangkuk-polimetakrilamida (kitosan-g-PMAM) telah dicirikan menggunakan spektrometri inframerah transformasi Fourier (FTIR), ¹³C NMR keadaan pepejal, analisis termogravimetri (TGA), kalorimetri imbasan kebedaan (DSC) dan mikroskopi imbasan elektron (SEM). Faktor penting dalam kopempolimeran cangkuk seperti masa tindak balas, suhu dan kepekatan APS, MAM dan kitosan telah dikaji dan dioptimum bagi memperoleh parameter cangkukan maksima. Peratus cangkukan dan perolehan tertinggi diperolehi dengan keadaan berikut: kitosan (1 g), MAM (4 g), APS (0.6 g), masa tindak balas (4 j) dan suhu (70°C).

Kata kunci: Ammonium persulfat; kitosan; kopempolimeran cangkuk; metakrilamida; radikal bebas

INTRODUCTION

Considerable attention has been paid on chemical modification of natural polymers in the past few years. Among the modifications reported (e.g. nitration, phosphorylation, acylation, Schiff's base formation and alkylation (Zohuriaan-mehr 2005)), grafting method is a highly promising approach as it can introduce new properties to a polysaccharide with small loss of initial properties of the substrate. Grafted copolymer has broadened the field of natural polymers' application by choosing different types of side chains. There are several techniques of grafting such as chemical, radiation, photochemical, plasma-induced techniques and enzymatic grafting (Bhattacharya & Misra 2004). In free radical grafting, chemical initiator is used to produce radicals that can be transferred to the substrate and react with monomers in order to form copolymer graft.

Chitosan, an amino containing biopolymer and the second most abundant polysaccharide in nature after cellulose, is a derivative of chitin which can be prepared with a strong alkaline solution. It is mainly composed of

β -(1,4) linked 2-deoxy-2-amino-D-glucopyranose units and partially of β -(1,4) linked 2-deoxy-2-acetamido-D-glucopyranose (Figure 1) (Islam et al. 2011). Owing to its fascinating properties such as biodegradability, biocompatibility and nontoxic nature, chitosan can be used in many fields including cosmetics, textile industry, foods processing, agriculture and water treatment (Cheba 2011). This basic polysaccharide also has been investigated in the manufacture of paper (Zakaria et al. 2015) and stabilizer in synthesis of metal nanoparticles for biomedical applications (Ahmad et al. 2014; Akmaz et al. 2013). Recently, studies on the graft copolymerization of chitosan with various vinyl monomers have been extensively conducted to explore fully their high potential. Chitosan grafted with styrene using APS as initiator was successfully prepared by our research group (Al Sagheer et al. 2013). Similarly, chitosan-g-poly(2-hydroxyethyl acrylate) was carried out in aqueous solution using APS (Mun et al. 2008). Peroxydisulfate and ascorbic acid were used as redox initiator to graft methyl methacrylate onto chitosan (Singh et al. 2009a). Graft copolymer of chitosan with acrylamide

was also reported using the same initiating system (Singh et al. 2009a). In another work, graft copolymerization of chitosan with caffeic and ferulic acids was prepared by the addition of ascorbic acid and hydrogen peroxide (Liu et al. 2014). The literature survey, however, showed that no report has been published on the graft copolymerization of MAM onto chitosan using APS initiating system. In this article, we report the optimized APS-initiated chitosan-g-PMAM and the influence of important parameters in the reaction. The properties of pure chitosan and grafted chitosan were examined in details.

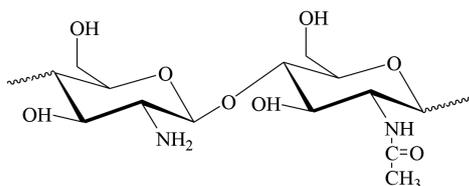


FIGURE 1. Structure of chitosan

MATERIALS AND METHODS

MATERIALS

Chitosan (medium molecular weight), methacrylamide and ammonium persulfate were purchased from Sigma-Aldrich (St. Louis, USA). Acetone and methanol were from QRĕc (Selangor, Malaysia). All reagents and chemicals were used directly without further purification.

GRAFT COPOLYMERIZATION

Graft copolymerization of methacrylamide on chitosan was carried out under homogenous conditions. In typical reaction, chitosan was dissolved in 1% acetic acid (100 mL) and placed in a 250 mL three-necked flask fitted with a reflux condenser, magnetic stirrer and a gas inlet system. A known amount of APS in 10 mL of distilled water was mixed with chitosan solution under a nitrogen gas flow for 30 min. The mixture was heated at different temperatures ranging from 50 to 90°C. After that, MAM solution (20 mL) was added and continuously stirred for polymerization. The reaction was stopped by letting air into the reactor. The grafted copolymer was precipitated in cold acetone and separated by filtration, dried in a vacuum oven and weighed. To remove any polymethacrylamide (PMAM) homopolymer, the crude product was washed with methanol by Soxhlet extraction overnight. Pure chitosan-g-PMAM was collected using simple filtration and dried to reach a constant weight.

All samples were completely dried before used for characterization. The grafting ratio $G(\%)$ and yield of graft copolymerization; $Y(\%)$ were evaluated as equations described below (Singh et al. 2006);

$$G(\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

$$Y(\%) = \frac{W_2 - W_1}{W_3} \times 100 \quad (2)$$

where W_1 is the original weight of chitosan; W_2 is the weight of washed grafted copolymer and W_3 is the weight of MAM monomer.

Fourier transforms infrared spectroscopy (FTIR) spectra of chitosan and grafted copolymers were recorded on a Perkin Elmer Spectrum™ 400 model (USA) in the range of 4000 - 400 cm^{-1} .

Nuclear magnetic resonance (^{13}C -NMR) spectroscopy was conducted on both chitosan and chitosan-g-PMAM. Solid-state ^{13}C -NMR spectra were recorded on a Bruker Avance III HD spectrometer operating at ^{13}C resonance frequency of 100.6 MHz using a solid-state ^{13}C cross-polarization magic angle spinning (CP/MAS) with a 4-mm resonance probe head.

Thermogravimetric analysis (TGA) of chitosan and that of the chitosan-g-PMAM were carried out with a Q500 TA Thermal Analysis Instrument (Delaware, USA). The study was conducted in an inert atmosphere from 50°C to 800°C at a heating rate of 20°C min^{-1} .

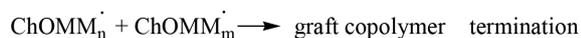
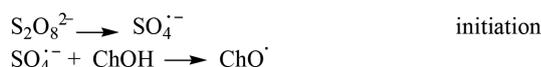
Differential scanning calorimetry (DSC) analysis was carried out using a Q2000 TA Thermal Advantage Instrument (Delaware, USA) using aluminium pan under a 50 mL min^{-1} nitrogen flow at heating rate of 20°C min^{-1} on the second heating of a heating-cooling-heating cycle. The surface morphology of ungrafted and grafted chitosan before and after Soxhlet extraction, were examined using a JEOL JSM 6390LVSEM (Tokyo, Japan). Before SEM observation, the powder form samples were fixed on aluminium stubs and coated with gold using auto fine coater (JFC-1600 model).

RESULTS AND DISCUSSION

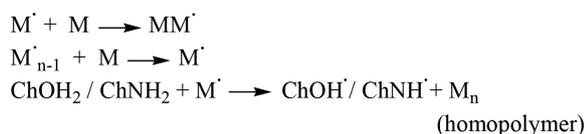
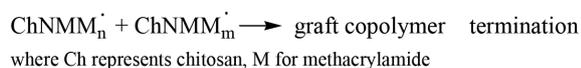
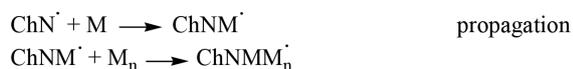
SYNTHESIS AND MECHANISM

A feasible mechanism of chitosan-g-PMAM using ammonium persulfate initiator is proposed (Scheme 1). At the stage of initiation, the persulfate initiator is decomposed under heating to generate sulfate ion radicals, which abstract hydrogen atom of hydroxyl at C6 and amine group at C2 of chitosan and hence, producing macroradicals. However, some researchers claimed that initially formed sulfate ion reacts with water to form hydroxyl ion and initiate active sites on polymeric backbone (Bhattacharya & Misra 2004). It is even more reactive than sulfate ion (Misra et al. 1984). The chitosan macroradicals then react with the monomers that are in close vicinity of the reaction sites and give propagating chains. These chains are terminated by combination to form graft copolymer.

Grafting at O–H groups of chitosan



Grafting at N–H groups of chitosan



SCHEME 1. Proposed mechanism of graft copolymerization

CHARACTERIZATION

The grafting of methacrylamide onto chitosan was characterized based on functional groups using FTIR technique. The IR spectra for chitosan, methacrylamide and chitosan-g-PMAM are presented in Figure 2. The results showed that the IR spectrum of chitosan has a strong peak around 3442 cm^{-1} due to O–H and N–H stretching vibrations of the polysaccharide (Singh et al. 2009a). A band representing C–H groups is seen at 2922 cm^{-1} . The stretching of carboxylate group (C=O) of chitosan appears at 1649 cm^{-1} . The signals depicted at 1424 and

1381 cm^{-1} correspond to the C–N bond stretching and deformation of C–H respectively (Mun et al. 2008; Singh et al. 2006a). MAM presents a broad band at 3405 cm^{-1} which are associated to N–H bond stretching. Typical bands of amide appear at 1633 and 1606 cm^{-1} , the first is related to stretching of the C=O group (amide I) and the second to N–H bond bending (amide II). MAM monomer also shows a peak at 1459 cm^{-1} that refers to CH_3 groups and another at 1410 cm^{-1} due to stretching of C–N bond. Meanwhile, the graft copolymer spectrum displays a combination of the bands found in both spectra of chitosan and MAM. A broad peak at 3432 cm^{-1} corresponds to a typical stretching for the O–H and N–H groups (Nandi et al. 2015). The variation in intensity and shifting of this band with respect to chitosan indicates that appreciable amounts of hydroxyl and amine groups of the polysaccharide have been participated in grafting reaction (Scheme 1). A band shown at 2932 cm^{-1} represents stretching of C–H bonds. Asymmetrical stretching of carboxylate C=O (amide I) is observed at 1659 cm^{-1} (Athawale & Padwaldesai 1999; Burfield & Ng 1978; Sadeghi et al. 2012). The grafting of MAM onto chitosan is further confirmed by characteristic absorption band at 1603 cm^{-1} due to amide II. Furthermore, bands at 1488 and 1390 cm^{-1} represent C–N bond stretching and deformation of CH_3 , respectively.

Both chitosan and chitosan-g-PMAM were further characterized by solid state ^{13}C Carbon NMR. From the spectrum of chitosan (Figure 3(a)), peaks at $\delta 23$ and $\delta 174$ were assigned to methyl and carbonyl groups of *N*-acetylglucosamine unit, respectively. The other peaks in the $\delta 56$ – 105 region can be attributed to the distribution of anomeric carbons, carbons attached to amino group and other carbons of polysaccharide (Al Sagheer et al. 2013; Heux et al. 2000; Liu et al. 2014). After the introduction of side chains, the spectrum (Figure 3(b)) shows additional signals at $\delta 16$ and $\delta 45$ which correspond to a-methyl and quaternary carbons of PMAM grafts, respectively (Don & Chen 2005; Konaganti et al. 2010). Also, the line width of chitosan at 174 was relatively enlarged due to formation of carbonyl of MAM (Hatada et al. 1983; Singh et al. 2009b).

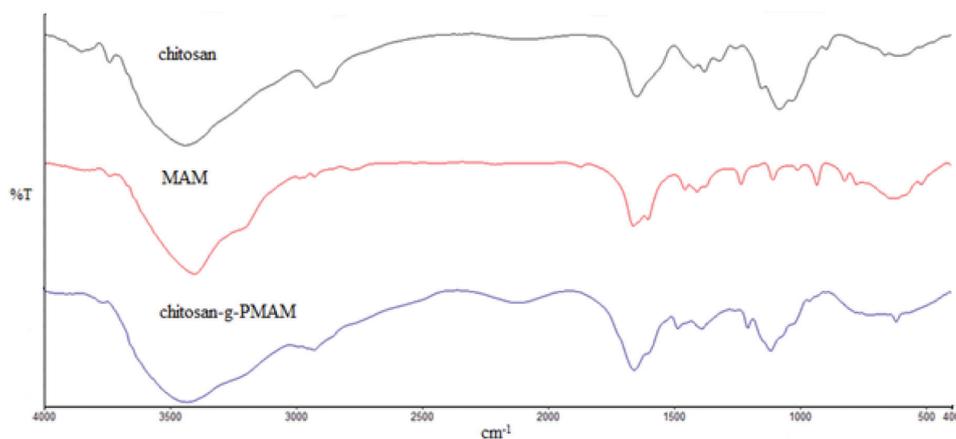


FIGURE 2. FTIR spectra of chitosan, MAM and chitosan-g-PMAM

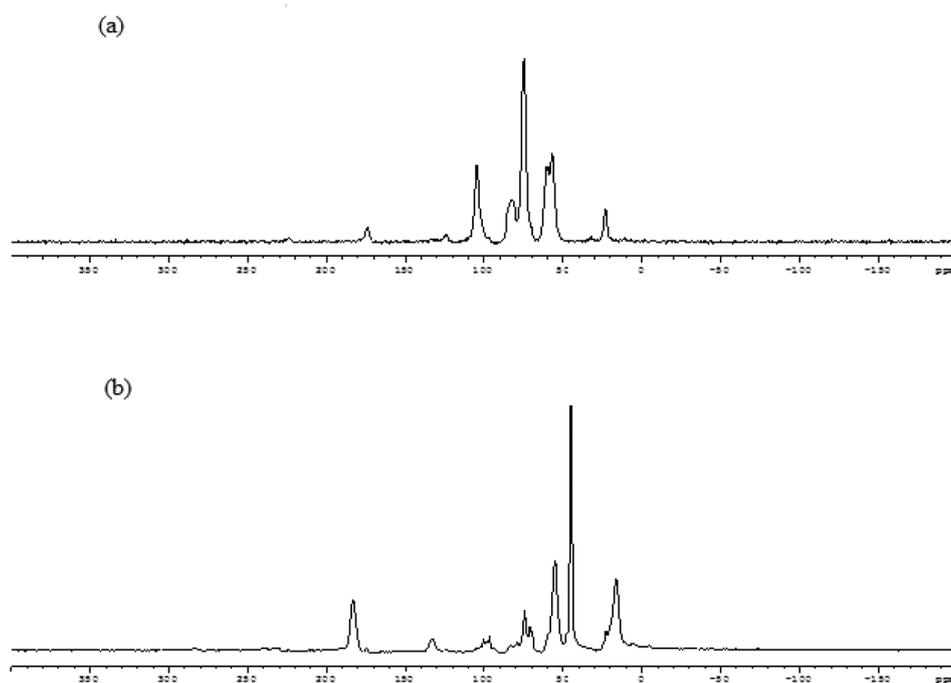


FIGURE 3. Solid state ^{13}C NMR spectra for chitosan (a) and chitosan-g-PMAM (b)

Thermal properties of chitosan and its grafted product were determined by TGA. As shown in Figure 4, pure chitosan exhibited two distinct stages. The initial weight loss of 9.9% observed in the range of 30 to 158°C is ascribed to elimination of moisture adsorbed to the polysaccharide. In the second stage, the weight loss (47.9%) was started at 230°C which attributed to the degradation of glycosidic bond of chitosan. The temperature of 50% weight loss of polysaccharide was found at 356°C (Al-Karawi et al. 2011) using potassium persulfate (PPS). On comparing to chitosan, chitosan-g-PMAM showed three degradation stages. The first stage ranged from 60 to 255°C (14.9%) contributing to the evaporation of free water. About 27.6% weight loss

of grafted copolymer began at 435°C. It probably indicated the depolymerization of chitosan backbone chain. There was 33.4% weight loss in the third stage from 435 up to 750°C which could be due to decomposition of chitosan-g-PMAM (Athawale & Padwaldeai 1999). 50% weight loss of grafted chitosan occurred at 408°C which is higher compared to pristine chitosan. Besides the confirmed success of grafting reaction, it also can be concluded that thermal stability of chitosan has been improved through grafted MAM.

The result of DSC analysis of grafted chitosan is illustrated in Figure 5. A broad endothermic peak at around 100°C was due to loss in moisture content. The

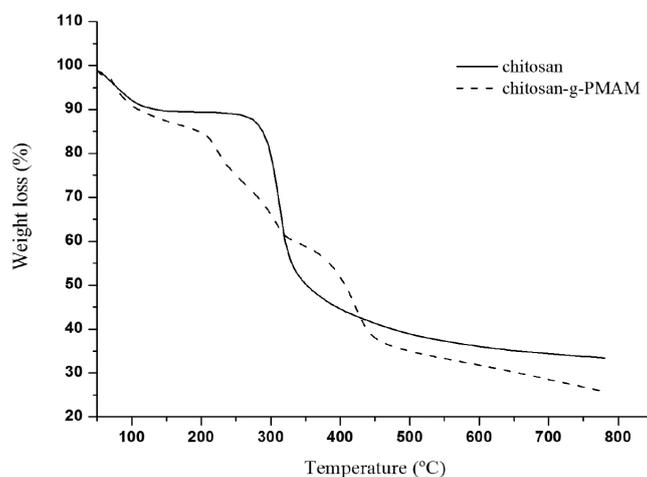


FIGURE 4. TGA thermograms of chitosan and chitosan-g-PMAM

glass transition temperature (T_g) of chitosan-g-PMAM was found at 253°C, which was higher than that of normal PMAM (which is about 250°C) (Kuo et al. 2003)000 Da. Polystyrene-b-poly(ferrocenylisopropylmethylsilane). The affected value after graft copolymerization indicated the existence of independent PMAM in the copolymers since there was no T_g value of native chitosan that can be observed as it is made up of rigid structures. Similar observation was reported in other studies (Don & Chen 2005; Shanmugapriya 2011; Stawski & Połowiński 2005). Another small endothermic peak recorded at 296°C was referred to melting transition (T_m) point of graft copolymer.

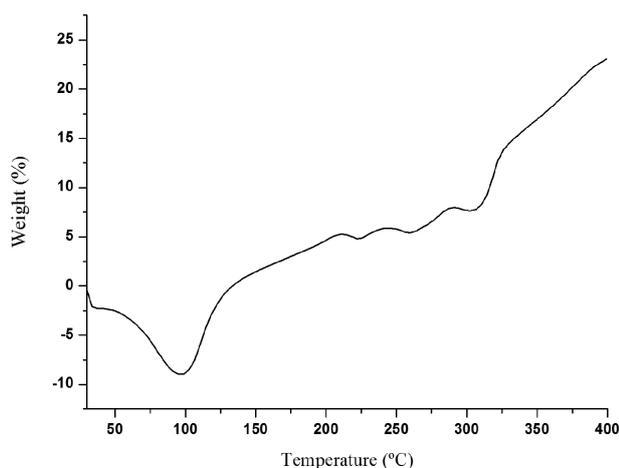


FIGURE 5. DSC curve of chitosan-g-PMAM

Figure 6 represents SEM images of chitosan and its grafted product at 10,000 magnification. It can be clearly seen that, the polysaccharide shows smooth surface with no pores or semi-pores on the surface as it has a strong inter and intra hydrogen bondings (Stawski & Połowiński 2005). Graft copolymerization with MAM has effectively modified the surface morphology of chitosan to become spherulites-like structure which provided larger surface area. Moreover, it was showed that the characteristic of pristine chitosan has been changed specifically to a better adsorbent.

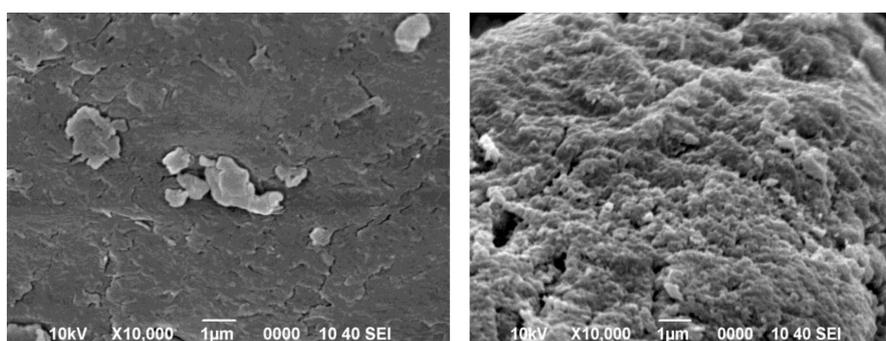


FIGURE 6. Surface morphology of chitosan (left) and chitosan-g-PMAM (right)

OPTIMIZATION OF REACTION CONDITIONS

The graft reaction conditions were investigated in detail to obtain a high grafting ratio and yield percentage, including the temperature, time reaction, initiator concentration, monomer concentration and concentration of substrate.

EFFECT OF TEMPERATURE REACTION

Graft copolymerizations of chitosan and methacrylamide were carried out at different temperatures in the range of 50-90°C while keeping other variables constant. From the results, it was clear that both grafting and yield percentages steadily increased with the increase in polymerization temperature up to 70°C (Figure 7). This behavior corresponds to the fact that high temperature favours the activation of molecules and accelerates their mobility in the solution which in turn enhances the diffusion of monomers onto the chitosan backbone. The subsequent trend of almost levelling off with further increase in temperature of above 70°C could be a result of progressive collision between molecules and thus leading to an early chain termination. The highest G (%) and Y (%) evaluated were found to be 290.8% and 96.9%, respectively.

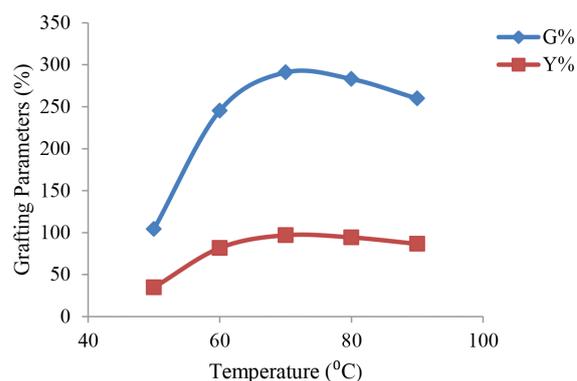


FIGURE 7. Effect of temperature on the grafting parameters

EFFECT OF TIME REACTION

Figure 8 represents the effect of time of reaction on grafting parameters of chitosan-g-PMAM. In this investigation, polymerization time was changed between 2 and 6 h

while the temperature, chitosan, monomer and initiator concentration were kept constant. From the results, the grafting parameters increased steadily with reaction time of up to 4 h. The best percentages for grafting and yield obtained were 290.8 % and 96.9 %, respectively. The lowering of percentages by at reaction times of above 4 h could be associated with the high possibility of chain transfer reaction and premature termination. It can also relate to the fact that extending the duration could reduce the active sites on chitosan as well as the concentration of monomer and initiator.

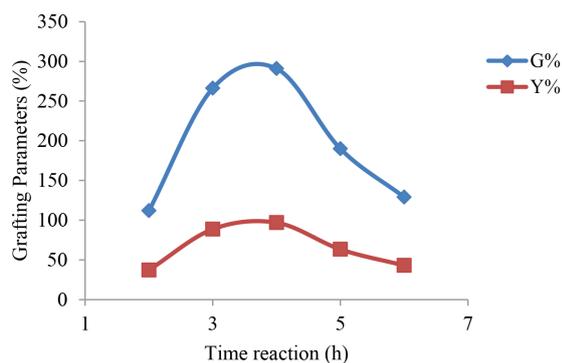


FIGURE 8. Effect of time reaction on grafting parameters

EFFECT OF APS CONCENTRATION

The influence of initiator concentration on graft copolymerization was studied by varying the concentration of APS in the range of 17.5×10^{-2} - 43.8×10^{-2} M. The results obtained are summarized in Figure 9. It was observed that the optimum values for grafting ratio (428.7%) and yield percentage (107.2%) were achieved at 26.3×10^{-2} M. As the concentration of initiator increases, the macroradicals generated for the saccharide unit of chitosan also increases thereby promoting the grafting copolymerization. However, beyond this value, grafting parameters were found to decrease continuously. This can be explained from the possibility that a further increase in APS concentration led to an excess of primary radicals in solution which could interact with the propagating chains and retard the reaction. In addition, there was no product obtained when 0.2 g of APS was used.

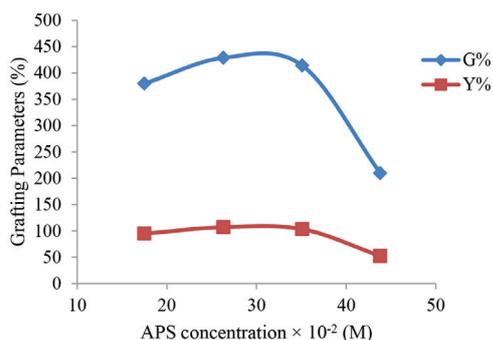


FIGURE 9. Effect of APS concentration on grafting parameters

EFFECT OF METHACRYLAMIDE CONCENTRATION

The monomer concentration has a remarkable effect on grafting parameters of chitosan-g-PMAM. To investigate this, different amounts of methacrylamide (2-6 g) were dissolved in 20 mL of distilled water with all other conditions kept constant. As shown in Figure 10, the grafting parameters initially increased gradually to a point but then decreased to some extent with further increase in monomer content. This is ascribed to the fact that more methacrylamide monomer molecules are present to graft with the macroradicals and thus increasing the rate of grafting. On the other hand, excessive MAM would result an adverse effect because of reduction in the active sites of chitosan backbone and subsequently inhibited graft copolymerization. Moreover, higher MAM amounts also aided the dominant of homopolymerization rather than grafting onto chitosan. The highest grafting ratio was found to be 379.8% at monomer concentration of 0.47 M.

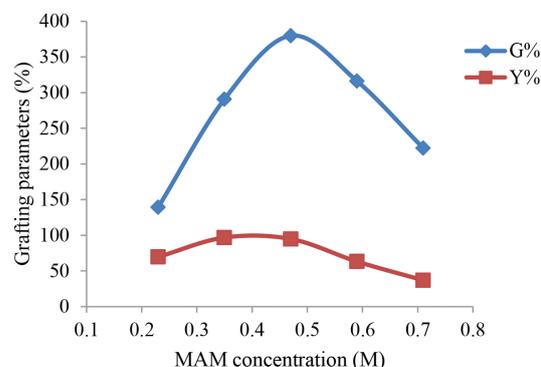


FIGURE 10. Effect of MAM concentration on grafting parameters

EFFECT OF CHITOSAN CONCENTRATION

The results of the graft copolymerization dependence on chitosan amount are shown in Figure 11. It can be seen that, percentage of grafting reached its maximum value at 624%. The increment of the percentage with increasing chitosan concentration could be due to availability of more grafting sites on the polymeric backbone accounting for more probability of methacrylamide attacking the chitosan. However, the percentage of grafting decreased upon further increase in chitosan amount beyond 0.5 g. This could be a result of the increase in viscosity of medium reaction which would restrict the movement of chitosan, methacrylamide and APS molecules hence, resulting in low graft copolymerization.

CONCLUSION

Modification of chitosan with MAM was successfully conducted using ammonium persulfate initiator. The presence of MAM structure in copolymer was confirmed by FTIR, solid state ^{13}C NMR and SEM. TGA and DSC analyses were used to examine the thermal properties

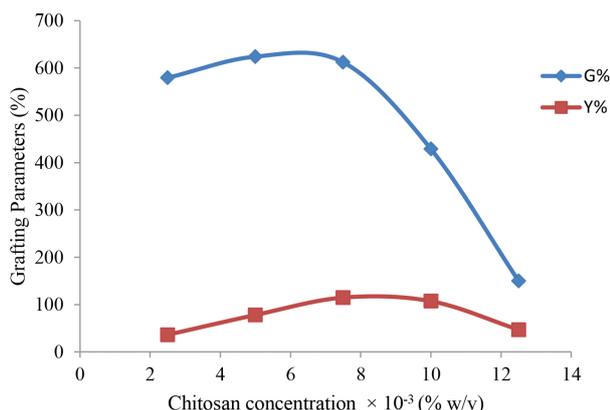


FIGURE 11. Effect of chitosan concentration on grafting parameters

for polysaccharide and grafted copolymer. The results showed that the thermal stability of chitosan after graft copolymerization was remarkably improved. The changes in characteristics of chitosan-g-PMAM with respect to chitosan suggest that the material has a great potential to be applied as adsorbent.

ACKNOWLEDGEMENTS

The authors wish to thank Universiti Teknologi Malaysia and the Ministry of Higher Education Malaysia (MOHE), Malaysia for facilitations and financial support through research grant number R.J130000.7809.4F177 and studentship for Zetty Azalea Sutirman.

REFERENCES

Ahmad, S.I., Radiman, S. & Ahmad, M.S. 2014. Sintesis nanozarah kuprum dalam larutan kitosan menggunakan kaedah sinaran gama. *Sains Malaysiana* 43(11): 1751-1759.

Akmaz, S., Dilaver Adgüzel, E., Yasar, M. & Erguven, O. 2013. The effect of ag content of the chitosan-silver nanoparticle composite material on the structure and antibacterial activity. *Advances in Materials Science and Engineering* 2013: 12-18.

Al-Karawi, A.J.M., Al-Qaisi, Z.H.J., Abdullah, H.I., Al-Mokaram, A.M.A. & Al-Heetimi, D.T.A. 2011. Synthesis, characterization of acrylamide grafted chitosan and its use in removal of copper(II) ions from water. *Carbohydrate Polymers* 83: 495-500.

Al Sagheer, F.A., Khalil, K.D. & Ibrahim, E.I. 2013. Synthesis and characterization of chitosan-g-poly(2-(furan-2-carbonyl)-acrylonitrile): Grafting of chitosan using a novel monomer prepared by a Baylis-Hillman reaction. *European Polymer Journal* 49: 1662-1672.

Athawale, V.D. & Padwaldesai, M.P. 1999. Free radical graft copolymerization of methacrylamide onto agar. *European Polymer Journal* 35: 1237-1243.

Bhattacharya, A. & Misra, B.N. 2004. Grafting: A versatile means to modify polymers: Techniques, factors and applications. *Progress in Polymer Science (Oxford)* 29: 767-814.

Burfield, D.R. & Ng, S.C. 1978. Persulphate initiated graft copolymerization of methacrylamide in natural rubber latex E --III. 14: 799-802.

Cheba, B.A. 2011. Chitin and chitosan : Marine biopolymers with unique properties and versatile applications. *Journal of Biotechnology & Biochemistry* 6: 149-153.

Don, T.M. & Chen, H.R. 2005. Synthesis and characterization of AB-crosslinked graft copolymers based on maleilated chitosan and N-isopropylacrylamide. *Carbohydrate Polymers* 61: 334-347.

Hatada, K., Kitayama, T. & Ute, K. 1983. Determination of tacticity of polymethacrylamide by C-13 NMR spectroscopy. *Polymer Bulletin* 9: 241-244.

Heux, L., Brugnerotto, J., Desbrières, J., Versali, M.F. & Rinaudo, M. 2000. Solid state NMR for determination of degree of acetylation of chitin and chitosan. *Biomacromolecules* 1: 746-751.

Islam, M., Masum, S., Rahman, M.M., Islam, A. & Shaikh, A.A. 2011. Preparation of chitosan from shrimp shell and investigation of its properties. *International Journal of Basic & Applied Sciences* 11(1): 77-80.

Konaganti, V.K., Kota, R., Patil, S. & Madras, G. 2010. Adsorption of anionic dyes on chitosan grafted poly(alkyl methacrylate)s. *Chemical Engineering Journal* 158: 393-401.

Kuo, S.W., Kao, H.C. & Chang, F.C. 2003. Thermal behavior and specific interaction in high glass transition temperature PMMA copolymer. *Polymer* 44: 6873-6882.

Liu, J., Wen, X.Y., Lu, J.F., Kan, J. & Jin, C.H. 2014. Free radical mediated grafting of chitosan with caffeic and ferulic acids: Structures and antioxidant activity. *International Journal of Biological Macromolecules* 65: 97-106.

Misra, B.N., Mehta, I.K. & Khetarpal, R.C. 1984. Grafting onto cellulose. VIII. Graft copolymerization of poly(ethylacrylate) onto cellulose by use of redox initiators. Comparison of initiator reactivities. *Journal of Polymer Science: Polymer Chemistry Edition* 22: 2767-2775.

Mun, G.A., Nurkeeva, Z.S., Dergunov, S.A., Nam, I.K., Maimakov, T.P., Shaikhutdinov, E.M., Lee, S.C. & Park, K. 2008. Studies on graft copolymerization of 2-hydroxyethyl acrylate onto chitosan. *Reactive and Functional Polymers* 68: 389-395.

Nandi, G., Patra, P., Priyadarshini, R., Kaity, S. & Ghosh, L.K. 2015. Synthesis, characterization and evaluation of methacrylamide grafted gellan as sustained release tablet matrix. *International Journal of Biological Macromolecules* 72: 965-974.

Sadeghi, M., Ghasemi, N. & Soliemani, F. 2012. Graft copolymerization methacrylamide monomer onto carboxymethyl cellulose in homogeneous solution and optimization of effective parameters. *World Applied Sciences Journal* 16: 119-125.

Shanmugapriya, A. 2011. Optimization of ceric ammonium nitrate initiated graft copolymerization of acrylonitrile onto chitosan. *Journal of Water Resource and Protection* 03: 380-386.

Singh, V., Sharma, A.K. & Sanghi, R. 2009a. Poly(acrylamide) functionalized chitosan: An efficient adsorbent for azo dyes from aqueous solutions. *Journal of Hazardous Materials* 166: 327-335.

Singh, V., Sharma, A.K., Tripathi, D.N. & Sanghi, R. 2009b. Poly(methylmethacrylate) grafted chitosan: An efficient adsorbent for anionic azo dyes. *Journal of Hazardous Materials* 161: 955-966.

Singh, V., Tiwari, A., Tripathi, D.N. & Sanghi, R. 2006a. Microwave enhanced synthesis of chitosan-graft-polyacrylamide. *Polymer* 47: 254-260.

- Singh, V., Tiwari, A., Pandey, S. & Singh, S.K. 2006b. Microwave-accelerated synthesis and characterization of potato starch-g-poly(acrylamide). *Starch/Staerke* 58: 536-543.
- Stawski, D. & Połowiński, S. 2005. Polymerization of itaconic acid. *Polimery/Polymers* 50: 118-122.
- Zakaria, S., Chin, H.C., Wan Ahmad, W.H., Kaco, H., Soon, W.C. & Chin, H.C. 2015. Mechanical and antibacterial properties of paper coated with chitosan. *Sains Malaysiana* 44(6): 905-911.
- Zohuriaan-mehr, M.J. 2005. Advances in chitin and chitosan modification through graft copolymerization: A comprehensive review. *Polymer Journal* 14: 235-265.

Zetty Azalea Sutirman, Mohd Marsin Sanagi*
Ahmedy Abu Naim, Khairil Juhanni Abd Karim &
Wan Aini Wan Ibrahim
Department of Chemistry, Faculty of Science
Universiti Teknologi Malaysia
81310 UTM Johor Bahru, Johor Darul Takzim
Malaysia

Mohd Marsin Sanagi*
Centre for Sustainable Nanomaterials
Ibnu Sina Institute for Scientific and Industrial Research
Universiti Teknologi Malaysia
81310 UTM Johor Bahru, Johor Darul Takzim
Malaysia

*Corresponding author; email: marsin@kimia.fs.utm.my

Received: 11 September 2015

Accepted: 28 July 2016