Carbohydrate Polymers 98 (2013) 1618–1623

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Chemical modification of chitin by grafting with polystyrene using ammonium persulfate initiator

Ahmedy Abu Naim[a,*], Abdulganiyu Umar[a], Mohd Marsin Sanagi[b], Noraimi Basaruddin[a]

[a] Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b] Ibnu Sina Institute for Fundamental Science Studies, Nanotechnology Research Alliance, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

ARTICLE INFO

Article history:
Received 30 May 2013
Received in revised form 22 July 2013
Accepted 23 July 2013
Available online 31 July 2013

Keywords:
Chitin
Polystyrene
Ammonium persulfate
Graft copolymer
Radical polymerization

ABSTRACT

Chitin was successfully grafted with polystyrene by free radical mechanism using ammonium persulfate (APS) initiator. The reaction was carried out in aqueous medium. The effect of pH, chitin:monomer weight ratio, APS, reaction time and reaction temperature were investigated. The results showed that the optimum conditions for grafting of polystyrene were found as follows: pH 7, chitin:monomer weight ratio of 1:3, 0.4 g of APS, reaction temperature of 60 °C and reaction time 2 h. The graft copolymer was characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis (TGA) and differential scanning electron microscopy (DSC). Gel permeation chromatography (GPC) analysis carried out on the hydrolyzed graft copolymer showed that the M_n and M_w were 6.3395×10^4 g/mol and 1.69283×10^5 g/mol, respectively, with polydispersity index of 2.7.

1. Introduction

Chitin is the second most abundant biopolymer (after cellulose) and is known to be the only natural basic polysaccharide widely found in nature (Muzzarelli et al., 2012). Chitin and its deacetylated form chitosan, are bio-renewable, biodegradable, biocompatible, inexpensive and environmentally friendly polymers. Chitin is a heteropolymer made up of β-(1 → 4)-2-acetamido-2-deoxy-β-D-glucopyranose units. It is found in nature as the exoskeleton of marine invertebrates, but mainly extracted from crab and shrimp shells of waste materials from the seafood processing industries (Lin, Lin, & Chen, 2009; Liu et al., 2010). The chemistry of chitin is quite interesting due to the presence of hydroxyl groups at C3 and C6 and acetamide group at C2 positions that makes it more useful than cellulose. As such, chemical modification of this biopolymer can result in special polymeric material having distinct functionality with numerous applications, such as in the field of chromatography, textile industries, cosmetics and toiletries, as biodegradable, chelating agent as well as biomedical material (Cho, Jang, Park, & Ko, 2000; Muzzarelli et al., 2012).

Despite all these fascinating properties, chitin has remained under-utilized biopolymer primarily due to its insolubility in all usual solvents (Chang, Chen, & Zhang, 2011; Pillai, Paul, & Sharma, 2009). This insolubility is due to its intra and inter-molecular hydrogen bonds. Chemical modification of chitin is an important aspect which continues to receive considerable attention. Graft copolymerization is one of such modification modes.

Graft copolymerization of chitin has been reported previously. Chitin grafted with styrene copolymer using mercaptochitin as initiator was reported by a group of researchers (Kurita, Hashimoto, Yoshino, Ishii, & Nishimura, 1996). Graft copolymerization of styrene onto chitin and chitosan by radiation-induced technique was also reported (Pengfei, Maolin, & Jilan, 2001; Shigano, Kondo, & Takemoto, 1982). Graft copolymerization of γ-methyl L-glutamate N-carboxy anhydride (NCA) onto water-soluble chitin in water/ethyl acetate system (with side chains of various lengths) was successfully prepared (Kurita, Yoshida, & Koyama, 1988). Methyl methacrylate was grafted onto mercaptochitin using dimethyl sulfoxide as a solvent, and was then successfully converted into chitin-graft-(PMMA-co-poly(sodium methacrylate)) (Kurita, Inoue, & Harata, 2002). Graft copolymerization of styrene onto iodochitin in a fairly dissolved and highly swollen state was also reported using both cationic and radical mechanism (Kurita et al., 1992). Fenton's reagent as redox initiator was also introduced to graft acrylic acid and acrylonitrile onto chitin/chitosan (Aly, Jeon, & Park, 1997).

Acrylic acid was grafted onto β-chitin by forming an ester linkage between carboxylic groups of acrylic acid and hydroxyl group by the addition of potassium peroxydisulfate initiator. Acrylic acid was grafted onto partially deacytylated chitin using radiation

* Corresponding author. Tel.: +60 75534462; fax: +60 75566162.
E-mail address: ahmedy@kimia.fs.utm.my (A. Abu Naim).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.07.054

mechanism (Hien, Van Phu, Duy, & Huy, 2005). Chitin was grafted with succinic anhydride using 4-dimethylaminopyridene as catalyst (Yoshimura, Uchikoshi, Yoshiura, & Fujioka, 2005). Thiolated β-chitin was sequentially modified to 6-mercaptochitin and then poly(methyl methacrylate) was grafted onto the derivative (Munro, Hanton, Moratti, & Robinson, 2009). Sulfated chitin was prepared using sulfur trioxide-pyridine in 5% LiCl/DMAc solvent system (Zou & Khor, 2009). Recently, acrylic acid was grafted onto chitin nanofibre, using potassium persulfate as a radical initiator (Ifuku, Iwasaki, Morimoto, & Saimoto, 2012) and homogenous synthesis of chitin-based acrylate copolymer using ammonium persulfate initiator (Liu et al., 2013) were reported. All these reported modifications involved either the elimination of OH group on the C6 or modifying the acetamido group at C2 of the glucosamine and thus far, no report has described on the investigation of pH in relation to chemical reaction of chitin. In the present work, we report for the first time the chemical modification of chitin by grafting with polystyrene using ammonium persulfate (APS) as initiator.

2. Materials and methods

2.1. Materials

Styrene monomer was purchased from Acros (New Jersey, USA). Chitin from crab shells was purchased from Sigma–Aldrich (St. Louis, USA), chloroform from BrightChem (Penang, Malaysia), ether anhydrous from J.T Baker, acetone and ethyl benzene from Sigma–Aldrich (St. Louis, USA), and methanol from QRëc (Selangor, Malaysia). All reagents and solvents were analytical grade, and were used directly as received without further purification except styrene.

2.2. Preparation of chitin solution

The chitin solution was prepared as described previously (Liu et al., 2009; Sannan, Kurita, & Iwakura, 1975, 1976) with a little modification. Instead of considering pH 7–8 alone as previously reported, the grafting was performed at various pH 5–8 in order to determine the pH that will give the highest percentage grafting. Dry chitin powder was soaked in concentrated sodium hydroxide solution (40%, w/w) and leave to stand at 29 °C and 760 mmHg pressure for 65 h to form a viscous brown suspension. The suspension was poured onto crushed ice (80 g) which was made from distilled water. Concentrated aqueous HCl was added dropwise to the mixture with stirring until the pH reached 12. The pH was adjusted to different pH values (5–8) by adding proper amount of HCl (0.1 M) to the solution. The solution was stirred at various reaction temperatures ranging from 40 to 80 °C.

The alkali chitin solutions prepared above were transferred to a 5-necked flask equipped with nitrogen inlet tube, reflux condenser, and mechanical stirrer. The system was purged with nitrogen, stirred at 420 rpm and heated at different temperatures ranging from 40 to 80 °C. Ammonium per sulfate was added to the above and interact with the chitin solution for 30 min before adding the monomer.

Copolymers of soluble chitin and styrene were prepared using different parameters namely chitin:monomer weight ratio, temperature, reaction time, pH of the chitin solution and initiator content with constant stirring at 420 rpm. The reaction mixture was poured into methanol to precipitate the crude copolymer. The precipitate was filtered using sintered glass funnel, dried under vacuum at 40 °C as tan powdery material until a constant weight was achieved. The crude graft copolymer was washed with ethyl benzene (Soxhlet extraction) for 24 h to remove any polystyrene present. The extracts were filtered using sintered funnel, washed with methanol to rinse the copolymer. The clean graft copolymers were dried to a constant weight in a vacuum oven at 40 °C.

The graft copolymer (1 g) was transferred into 100 mL round bottom flask fitted with condenser, which was immersed in an oil bath. Hydrochloric acid (6 M, 20 mL) was added into the above flask, and the mixture was magnetically stirred overnight at 90 °C. The hydrochloric acid, along with the degraded chitin was removed by simple filtration. Chloroform (40 mL) was added to the residue and the solution was concentrated under reduced pressure and poured into methanol to precipitate the cleaved polystyrene. The precipitate was filtered using sintered funnel, dried in a vacuum oven to a constant weight to give 0.7 g of polystyrene.

2.3. Characterization

After washing, the products were weighed and characterized by FT-IR (KBr), TGA, DSC and GPC. The percentage of grafting; G (%) and the yield of graft copolymerization; Y (%) were calculated using the equations described below (Blair & Kam Moon, 1982; Kaewtatip & Tanrattanakul, 2008):

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

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

where W_1 was the original weight of the chitin, W_2 was weight of washed product and W_3 was the weight of the styrene monomer. IR spectra were recorded on a Perkin-Elmer Spectrum-One FTIR Spectrometer. The number average molecular weight, weight average molecular weight and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) Waters 1515 and Waters 2414 RI detectors with a set of Styragel columns (HR3, HR4 and HR5, 7.8 × 300 mm). All measurements were carried out at 36 °C using THF as eluent with flow rate of 1.0 mL/min. The system was calibrated using polystyrene standards with the molecular weight range from 2.95×10^3 g/mol to 4.22×10^6 g/mol.

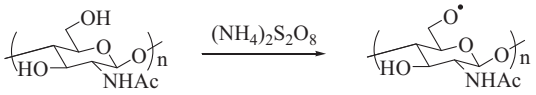
The glass transition point of the graft copolymer was analyzed with Thermal Advantage Instrument Q2000 with Tzero technology and refrigerated cooling system (RCS 90), using aluminium pan under a 50 mL/min N_2 flow at the heating rate of 20 °C/min on the second heating of a heating–cooling–heating cycle. A sample of approximately 10 mg was closed separately in sample pan with another empty pan placed on reference temperature sensor. The samples were scanned in the temperature range of 20–180 °C.

Thermogravimetric analysis (TGA) was performed by using TA Q500. A temperature calibration test was conducted by running calcium oxalate monohydrate sample as standard. The analysis was carried out with a temperature range of 50–600 °C at a heating rate of 10 °C/min.

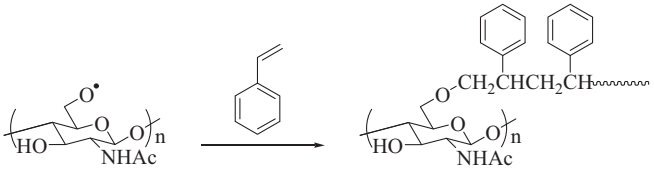
3. Results and discussion

3.1. Preparation of the graft copolymer

Generally, initiation of a free-radical polymerization is favoured by the production of free-radicals in the presence of the vinyl monomer. Although the initiating free-radicals can be generated directly from the monomer, it is more common for the active sites to be generated when initiator is added. It is well known that water-soluble initiators, such as ammonium persulfate can be decomposed thermally under suitable temperature to yield a pair of initiating radicals ($SO_4^{-\bullet}$). It is believed that, these primary radicals will be consumed by some alternative fast reactions, yet some of them will diffuse out of the solvent cage to abstract the hydrogen atom attached to the most easily accessible carbinol, thereby



Scheme 1. Reaction scheme for the generation of chitin macroradicals.



Scheme 2. Reaction scheme for the preparation of the chitin-*g*-PS copolymer.

generating an active site(s) that could be used to graft some vinyl monomer onto the backbone of cellulose-like biopolymers (Allcock, Lampe, & Mark, 2003: chap. 3).

The viscous alkali chitin solution dissolves gradually when poured onto crushed ice. This could be due to the role of ice played in braking the inter and inter-molecular hydrogen bonds, destroying the secondary structure of chitin while keeping its main structure (Liu et al., 2010). Macroradicals were generated on the backbone of chitin at oxygen atom as shown in Scheme 1. It is well known that some initiators such as persulfates dissociate into free radicals when heated, there by abstracting hydrogen either from the solvent (in this case water) or directly from the OH on the polymer backbone to generate a macroradical (Kaewtatip & Tanrattanakul, 2008).

Chitin macroradicals were treated with styrene to initiate graft copolymerization by radical mechanism (Scheme 2). The macroradicals attacked the double bonds of the styrene and generate radicals onto it which resulted to repeated processes (propagation). The resulting graft copolymer was precipitated by pouring into methanol and finally the precipitate was washed with ethylbenzene by Soxhlet extraction, to remove any polystyrene homopolymer.

Fig. 1 shows FTIR spectra of (a) virgin chitin and (b) the synthesized chitin-*g*-PS copolymer. The spectrum (b) indicate the presence of polystyrene peaks with IR-band intensities at 3150–3000 cm^{-1} (=C—H (aromatic)), 3000–2850 cm^{-1} (—C—H stretching (alkane)), 1660–1500 cm^{-1} (C=C aromatic) in addition to those of chitin at 3600–3200 cm^{-1} (O—H and N—H stretching) and1659 cm^{-1} due to C=O stretching. The chitin-*g*-polystyrene copolymer was produced as tan powdery substance. The preparation of graft copolymers was carried out with different percentage grafting *G* (%), and percentage yield *Y* (%) by considering the reaction parameters.

3.1.1. *Effect of polymerization temperature*

Reaction temperature has great role on copolymerization. The results obtained in Table 1 showed that graft copolymerization was favoured at temperature of 60 °C; as percentage grafting of 239.8% and percentage yield of 79.93% were achieved under this temperature. Higher temperature promotes decomposition of the initiator, which could lead to creating more active sites (radicals) on the backbone of the chitin molecule (Scheme 1). At temperature above 60 °C, the percentage grafting was reduced. This could be a result of the increase in conversion of initiator to free radicals which would promote termination of the growing radicals and could result to low

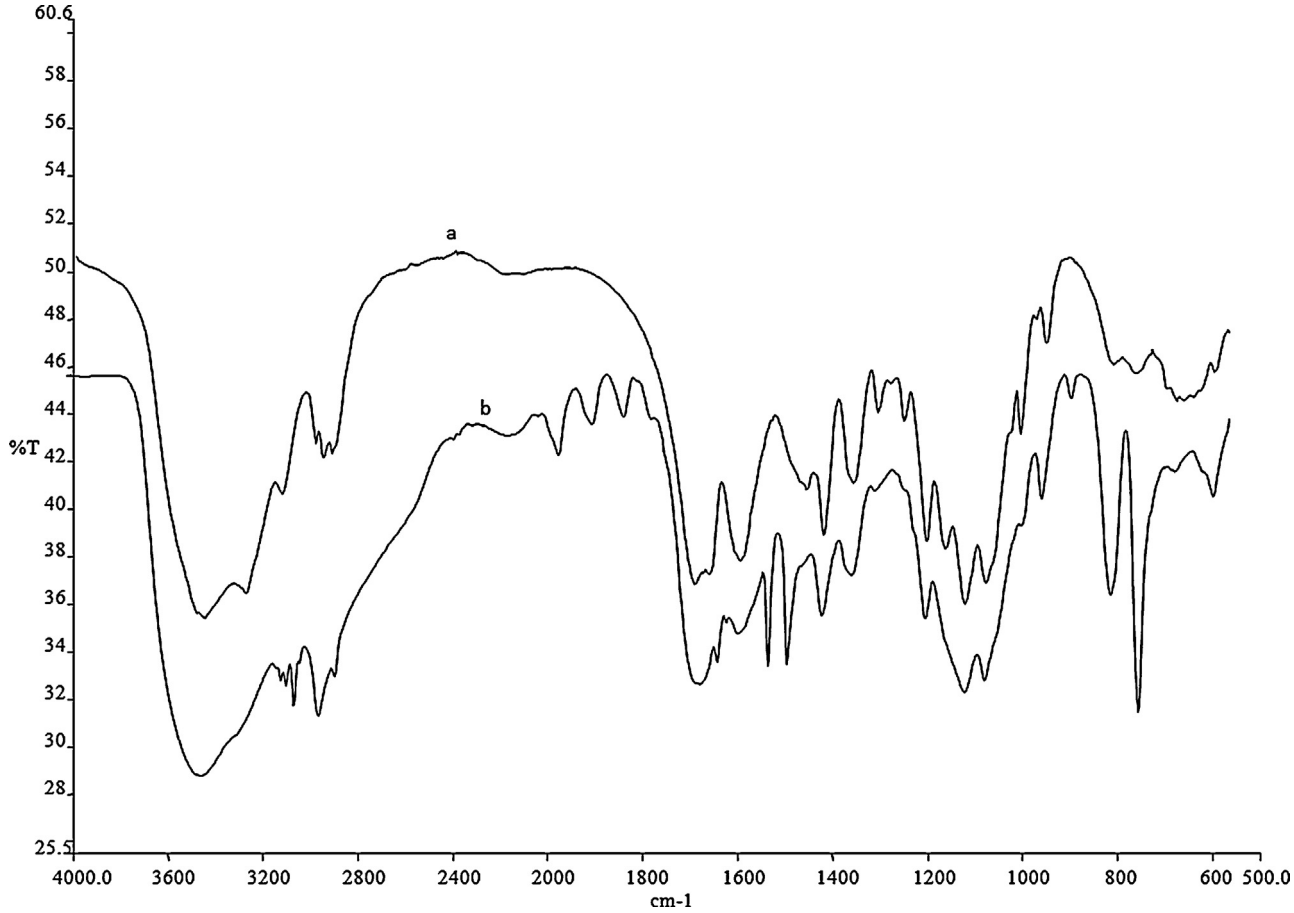


Fig. 1. The infrared spectra of (a) chitin sample (b) chitin-*g*-PS copolymer.

Table 1
Results of effect of polymerization parameters on the percentage grafting, *G* (%) and yield of copolymerization, *Y* (%) of samples polymerized at 2 h with ice water (80 g) and APS (0.4 g).

Chitin (g)	Styrene (g)	Temp (°C)	W_2 (g)[a]	*G* (%)[b]	*Y* (%)[c]
1	3	40	1.34	34.00	11.33
1	3	50	2.21	121.00	40.33
1	**3**	**60**	**3.398**	**239.80**	**79.93**
1	3	70	2.32	132.00	53.47
1	3	80	2.50	150.00	44.67
1	1	40	1.11	11.00	3.37
1	1	50	1.17	17.00	17.00
1	**1**	**60**	**1.67**	**67.00**	**67.00**
1	1	70	1.61	60.80	60.80
1	1	80	1.27	27.00	27.00
3	1	40	3.05	1.67	5.00
3	1	50	3.16	5.33	16.00
3	**1**	**60**	**3.44**	**14.67**	**44.00**
3	1	70	3.32	10.67	32.00
3	1	80	3.27	9.00	27.00

[a] W_2 represent weight of copolymer after Soxhlet extraction.
[b] *G* (%) represent percentage grafting.
[c] Y (%) represent yield of graft copolymerization.

molecular weight copolymer. This phenomena was also observed by other researchers (Nishioka, Matsumoto, & Kosai, 1983).

3.1.2. Effect of monomer concentration

The results (Table 1) also indicate that the amount of chitin and styrene monomer showed noticeable effects on *G* (%), hence the styrene rich system (3 g) was more suitable as it offered the highest *G* (%). This was also reported by other researchers in their works on starch (Fang, Fowler, & Hill, 2005; Kaewtatip & Tanrattanakul, 2008). Polymerization increases with increase in reasonable styrene monomer content; as more of monomer molecules will diffuse to the macroradical sites, and this will improve the *G*% and *Y*%. It is well known that higher monomer concentration aids the consumption of primary radicals, reducing the formation of cellulose macroradicals and decreasing the grafting efficiency and number of grafts (Nishioka, Minami, & Kosai, 1983).

3.1.3. Effect of the initiator concentration

Initiator is another vital parameter on graft copolymerization. To ascertain this, 1:3 weight ratio of chitin:styrene was polymerized at 60 °C for 2 h using APS as initiator in the range of (0.2–1.0 g by weight). The results (Table 2) show that both *G* (%) and *Y* (%)

Table 2
Effect of APS content on the percentage grafting, *G* (%) and percentage yield, *Y* (%) of copolymer, polymerized at 1:3 chitin:monomer ratio, 60 °C and ice water (80 g) for 2 h.

APS (g)[a]	W_2 (g)[b]	*G* (%)[c]	*Y* (%)[d]
0.2	1.240	12.40	4.13
0.4	**3.398**	**239.80**	**79.93**
0.6	1.750	75.00	25.00
0.8	1.110	11.00	3.67
1.0	1.083	8.30	2.77

[a] APS represent ammonium persulfate.
[b] W_2 represent weight of the copolymer after Soxhlet extraction.
[c] *G* (%) represent percentage grafting.
[d] *Y* (%) represent percentage yield.

increased with increase in APS content from 0.2 to 0.4 g, and then decreased due to increase in APS content. The decrease in grafting percentage and grafting efficiency at higher APS content could be attributed to the generation of more initiating radicals, and consequently increasing their chances to participate in either primary or secondary recombination with each other, or they may react with propagating polymer radicals or both; which could lead to termination (Nishioka, Matsumoto, et al., 1983). The maximum grafting percentage *G* (%), 239.8% and yield of copolymer *Y* (%), 79.93% were achieved from the system with

APS (0.4 g) as summarized in Table 2.

3.1.4. Effect of the reaction time on the polymerization

The reaction time was determined in the range of 1–4 h. The reaction was stopped by allowing air into the reaction vessel and then the reaction mixture was poured into methanol. It was observed that the reaction time of 2 h yielded the highest *G* (%) (239.8%) in chitin-*g*-PS copolymer as shown in Table 3. Longer reaction time would result to homopolymerization due to chain transfer and termination of the growing radicals. Since the grafting was manifested only on the surface of the trunk polymer granules as such, this has effect on the rate of graft copolymerization (Kaewtatip & Tanrattanakul, 2008).

3.1.5. Effect of pH on the polymerization

The highest percentage grafting and yield were obtained at pH 7 (Table 4). This could be due to sensitivity of the biopolymer towards pH. In a strong alkaline medium, active sites on the chitin backbone could not be generated. This could be due to the formation of

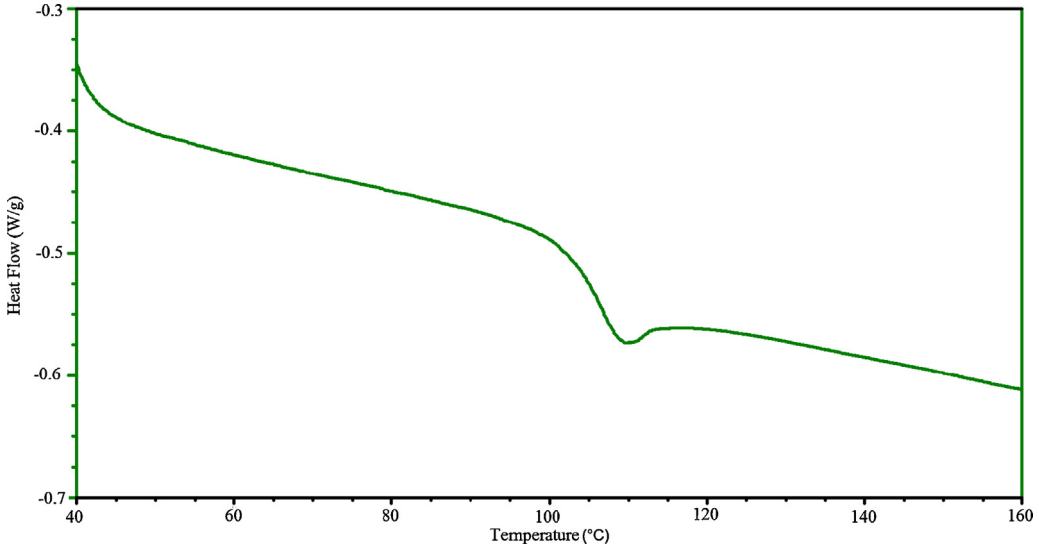


Fig. 2. DSC thermogram of the chitin-g-PS copolymer.

Table 3
Effect of reaction time on the percentage grafting, G (%) and percentage yield, Y (%), polymerized at 1:3 chitin:monomer weight ratio, 60 °C, APS (0.4 g) and ice water (80 g).

Time (h)	W_2 (g)[a]	G (%)[b]	Y (%)[c]
1	1.470	47.00	15.67
2	**3.398**	**239.80**	**79.93**
3	1.68	68.00	22.67
4	1.70	70.00	23.33

[a] W_2 represent weight of the copolymer after Soxhlet extraction.
[b] G (%) represent percentage grafting.
[c] Y (%) represent percentage yield.

Table 4
Effect of pH on the percentage grafting, G (%) and percentage yield, Y (%), polymerized at 1:3 chitin:monomer weight ratio, 60 °C, APS (0.4 g) and ice water.(80 g) for 2 h.

pH	G (%)[a]	Y (%)[b]
5	18	6.00
6	122	40.67
7	239.80	79.93
8	132	44.00

[a] G (%) represent percentage grafting.
[b] Y (%) represent percentage yield.

alkoxide ion, which is also a very strong base; and sodium ion occupied the position of hydrogen on the C6 hydroxyl group of the chitin (Khor, 2001: chap. 7). As such, it could be difficult for active sites to be generated.

3.1.6. Thermal properties of the graft copolymers

The differential scanning calorimetry (DSC) analysis signified the presence of T_g at around 109 °C due to atactic nature of the synthesized polystyrene (Fig. 2). The T_g values were higher than that of normal polystyrene, which is at about 100 °C since there was no indication of thermal transition points of chitin itself due to its rigid structure. The same phenomenon was also reported by other researchers (Kurita, Hashimoto, Yoshino, Ishii, & Nishimura, 1996).

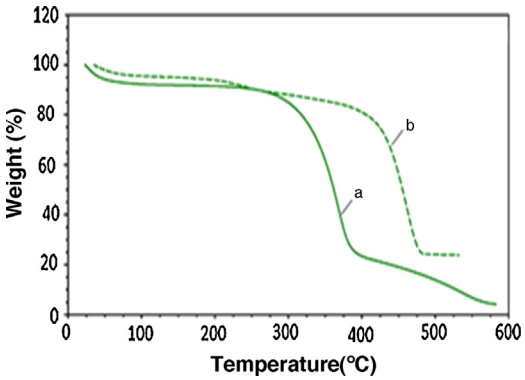
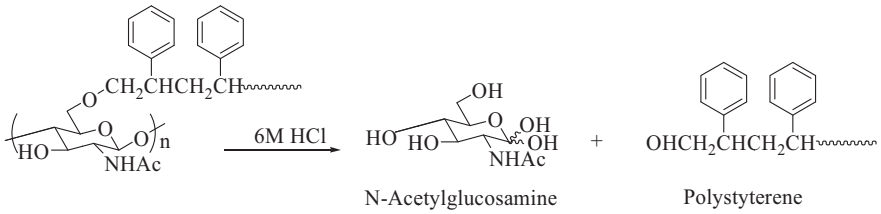


Fig. 3. TGA thermogram of (a) chitin and (b) chitin-g-PS.

The thermal properties of the original chitin and the graft copolymer were investigated by thermogarvimetric analysis (TGA). The copolymer showed higher stability compared to the chitin itself as shown in Fig. 3. The initial weight lost from 40 to 95 °C (8.39%) could be due to loss in moisture in chitin. There was a remarkable weight loss (69.36%) in chitin with the temperature from 280 to 389 °C. This could be due to breakage of C—O—C glycosidic bond as reported by other researchers (Liu et al., 2013). While for the graft copolymer, the weight loss was observed at higher temperature range, around 430–470 °C. There was further decrease in weight with increase in temperature to 600 °C, the chitin started to



Scheme 3. Reaction scheme for the hydrolysis of the copolymer.

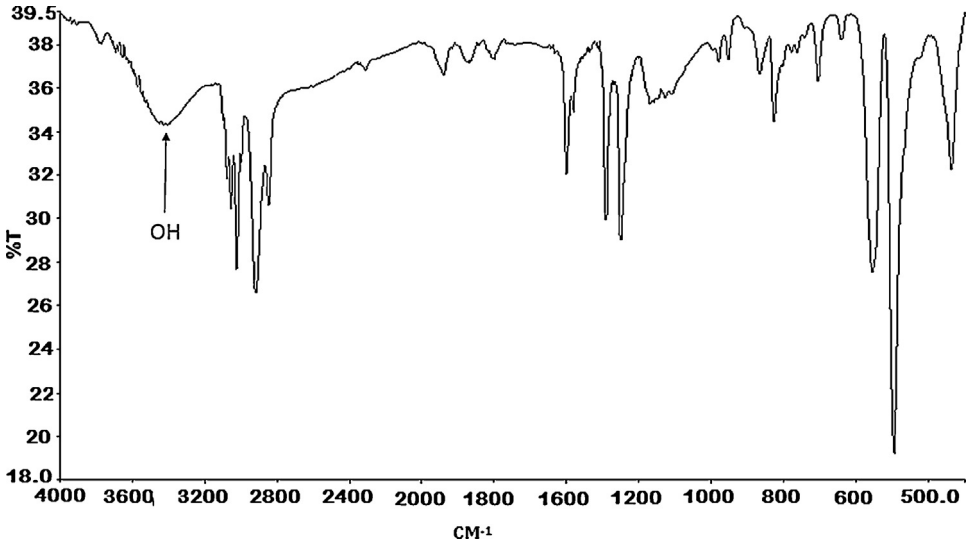


Fig. 4. FTIR spectrum of polystyrene from hydrolyzed chitin-g-PS copolymer.

decomposed at around 422 °C with 17.89% weight loss while the graft copolymers started to decompose at a temperature 475 °C with little ash compared to chitin.

3.1.7. Analysis of the side chains

To determine the molecular weight distribution of the isolated polystyrene, some graft copolymers were hydrolyzed with hydrochloric acid as shown in Scheme 3.

The IR spectrum of the hydrolyzed product resembles that of the linear polystyrene with terminal OH group at 3411 cm^{-1} (Fig. 4). GPC analysis revealed that the number-average molecular weight M_n and weight-average molecular weight M_w and of the isolated polystyrene were found to be 6.3395×10^4 g/mol and 1.69283×10^5 g/mol, respectively, with polydispersity index of 2.7. The broad molecular weight distribution could be due to uneven distribution of the side chains on the chitin backbone.

4. Conclusions

In this study, polystyrene was successfully grafted from oxygen atom of C6 of chitin by using ammonium persulfate initiator. The optimum conditions of grafting obtained were chitin (1 g) and styrene monomer (3 g), reaction temperature of 60 °C and reaction time of 2 h. The graft copolymer was characterized by FTIR technique. DSC analysis revealed the glass transition phenomena of the graft copolymer at a range of 106–109 °C. TGA results showed that the copolymer has higher thermal stability compared to chitin itself. Hydrolysis of the most grafted copolymer allowed isolation of polystyrene with M_n and M_w as 6.3395×10^4 g/mol and 1.69283×10^5 g/mol, respectively and polydispersity index of 2.7. We also have reported for the first time, the effect of pH on the reactivity of chitin in heterogeneous phase and the graft copolymerization hardly proceed in concentrated alkaline medium.

Acknowledgments

The authors are grateful to the Universiti Teknologi Malaysia and Ministry of Higher Education Malaysia (MOHE) for financial support through research grant [No. Q.J130000.2626.08J42] and research scholarship for Umar Abdulganiyu.

References

Allcock, H. R., Lampe, F. W., & Mark, J. E. (2003). *Contemporary polymer chemistry*. Upper Saddle River, NJ: Pearson Education/Prentice Hall.

Aly, A. S., Jeon, B. D., & Park, Y. H. (1997). Preparation and evaluation of the chitin derivatives for wastewater treatments. *Journal of Applied Polymer Science*, *65*(10), 1939–1946.

Blair, H. S., & Kam Moon, L. (1982). Graft copolymers of polysaccharides: 1. Graft copolymers of alginic acid. *Polymer*, *23*(12), 1838–1841.

Chang, C., Chen, S., & Zhang, L. (2011). Novel hydrogels prepared via direct dissolution of chitin at low temperature: Structure and biocompatibility. *Journal of Materials Chemistry*, *21*(11), 3865–3871.

Cho, Y.-W., Jang, J., Park, C. R., & Ko, S.-W. (2000). Preparation and solubility in acid and water of partially deacetylated chitins. *Biomacromolecules*, *1*(4), 609–614.

Fang, J. M., Fowler, P. A., & Hill, C. A. S. (2005). Studies on the grafting of acryloylated potato starch with styrene. *Journal of Applied Polymer Science*, *96*(2), 452–459.

Hien, N. Q., Van Phu, D., Duy, N. N., & Huy, H. T. (2005). Radiation grafting of acrylic acid onto partially deacetylated chitin for metal ion adsorbent. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*, *236*(1–4), 606–610.

Ifuku, S., Iwasaki, M., Morimoto, M., & Saimoto, H. (2012). Graft polymerization of acrylic acid onto chitin nanofiber to improve dispersibility in basic water. *Carbohydrate Polymers*, *90*(1), 623–627.

Kaewtatip, K., & Tanrattanakul, V. (2008). Preparation of cassava starch grafted with polystyrene by suspension polymerization. *Carbohydrate Polymers*, *73*(4), 647–655.

Khor, E. (2001). The chemistry of chitin as is known today. In *Chitin*. Oxford: Elsevier Science Ltd.

Kurita, K., Hashimoto, S., Yoshino, H., Ishii, S., & Nishimura, S. I. (1996). Preparation of chitin/polystyrene hybrid materials by efficient graft copolymerization based on mercaptochitin. *Macromolecules*, *29*(6), 1939–1942.

Kurita, K., Inoue, M., & Harata, M. (2002). Graft copolymerization of methyl methacrylate onto mercaptochitin and some properties of the resulting hybrid materials. *Biomacromolecules*, *3*(1), 147–152.

Kurita, K., Inoue, S., Yamamura, K., Yoshino, H., Ishii, S., & Nishimura, S. I. (1992). Cationic and radical graft copolymerization of styrene onto iodochitin. *Macromolecules*, *25*(14), 3791–3794.

Kurita, K., Yoshida, A., & Koyama, Y. (1988). Studies on chitin. 13. New polysaccharide/polypeptide hybrid materials based on chitin and poly(γ-methyl L-glutamate). *Macromolecules*, *21*(6), 1579–1583.

Lin, S.-B., Lin, Y.-C., & Chen, H.-H. (2009). Low molecular weight chitosan prepared with the aid of cellulase, lysozyme and chitinase: Characterisation and antibacterial activity. *Food Chemistry*, *116*(1), 47–53.

Liu, T., Li, B., Zheng, X., Liang, S., Song, X., Zhu, B., et al. (2010). Effects of freezing on the condensed state structure of chitin in alkaline solution. *Carbohydrate Polymers*, *82*(3), 753–760.

Liu, T., Qian, L., Li, B., Li, J., Zhu, K., Deng, H., et al. (2013). Homogeneous synthesis of chitin-based acrylate super absorbents in NaOH/urea solution. *Carbohydrate Polymers*, *94*(1), 261–271.

Liu, T. G., Li, B., Huang, W., Lv, B., Chen, J., Zhang, J. X., et al. (2009). Effects and kinetics of a novel temperature cycling treatment on the N-deacetylation of chitin in alkaline solution. *Carbohydrate Polymers*, *77*(1), 110–117.

Munro, N. H., Hanton, L. R., Moratti, S. C., & Robinson, B. H. (2009). Preparation and graft copolymerisation of thiolated β-chitin and chitosan derivatives. *Carbohydrate Polymers*, *78*(1), 137–145.

Muzzarelli, R. A. A., Boudrant, J., Meyer, D., Manno, N., DeMarchis, M., & Paoletti, M. G. (2012). Current views on fungal chitin/chitosan, human chitinases, food preservation, glucans, pectins and inulin: A tribute to Henri Braconnot, precursor of the carbohydrate polymers science, on the chitin bicentennial. *Carbohydrate Polymers*, *87*(2), 995–1012.

Nishioka, N., Matsumoto, K., & Kosai, K. (1983). Homogeneous graft copolymerization of vinyl monomers onto cellulose in a dimethyl sulfoxide-paraformaldehyde solvent system II. Characterization of graft copolymers. *Polymer Journal*, *15*(2), 153–158.

Nishioka, N., Minami, K., & Kosai, K. (1983). Homogeneous graft copolymerization of vinyl monomers onto cellulose in a dimethyl sulfoxide-paraformaldehyde solvent system III. Methyl acrylate. *Polymer Journal*, *15*(8), 591–596.

Pengfei, L., Maolin, Z., & Jilan, W. (2001). Study on radiation-induced grafting of styrene onto chitin and chitosan. *Radiation Physics and Chemistry*, *61*(2), 149–153.

Pillai, C. K. S., Paul, W., & Sharma, C. P. (2009). Chitin and chitosan polymers: Chemistry, solubility and fiber formation. *Progress in Polymer Science*, *34*(7), 641–678.

Sannan, T., Kurita, K., & Iwakura, Y. (1975). Studies on chitin, 1. Solubility change by alkaline treatment and film casting. *Die Makromolekulare Chemie*, *176*(4), 1191–1195.

Sannan, T., Kurita, K., & Iwakura, Y. (1976). Studies on chitin, 2. Effect of deacetylation on solubility. *Die Makromolekulare Chemie*, *177*(12), 3589–3600.

Shigano, Y., Kondo, K., & Takemoto, K. (1982). Functional monomers and polymers – 90. Radiation-induced graft polymerization of styrene onto chitin and chitosan. *Journal of Macromolecular Science: Chemistry*, *A17*(4), 571–583.

Yoshimura, T., Uchikoshi, I., Yoshiura, Y., & Fujioka, R. (2005). Synthesis and characterization of novel biodegradable superabsorbent hydrogels based on chitin and succinic anhydride. *Carbohydrate Polymers*, *61*(3), 322–326.

Zou, Y., & Khor, E. (2009). Preparation of sulfated-chitins under homogeneous conditions. *Carbohydrate Polymers*, *77*(3), 516–525.