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Graft Copolymerization of Methyl Methacrylate onto Alginate Using Benzoyl Peroxide Initiator.

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ABSTRACT

The graft copolymerization was carried out by methyl methacrylate with sodium alginate in which benzoyl peroxide (BPO) was used as initiator. It was found that the percentages of grafting and grafting yield were dependent on the concentration of methyl methacrylate (MMA), sodium alginate (NaAlg), BPO reaction temperature and reaction time. The optimum percentage of grafting was obtained when the concentration of BPO, MMA, and NaAlg were 4.13×10^{-3} mol L^{-1}, 7.99×10^{-1} mol L^{-1} and 1% w/v, respectively. The optimum reaction temperature and time were 80°C and 2 h, respectively. The graft copolymers were characterized by using FTIR spectroscopy, thermogravimetric analysis, scanning electron microscopy and solid-state ^{13}C-NMR spectroscopy. The plausible reaction mechanism of the graft copolymer formation using BPO initiating system has been proposed.

Keywords: benzoyl peroxide, optimization, methyl methacrylate, thermogravimetric analysis

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INTRODUCTION

Graft copolymerization of vinyl monomers onto natural polymers (polysaccharides) is a versatile method for preparing hybrid materials composed with synthetic polymers [1-2]. Because grafting enables the modification of many properties such as thermal resistance, sorbancy, ion-exchange capabilities and resistance to microbial attack [3-4]. Physico-chemical properties of graft copolymers have found to depend largely on different radical initiating systems [5-6]. Grafting can be done using redox ignitors [7], or by irradiation methods [8-9]. Alginate is a linear copolymer consisting mainly the residue of β-1,4-linked-D-mannuronic acid (M-Block) and α-1,4-linked-L-guluronic acid (G-Block). The residues exist in the form of homopolymer block (M-block, G-block) or heteropolymer block (MG-block) [9]. Sodium alginate (NaAlg) is readily soluble in aqueous media due its hydrophilic nature and also prone to enzymatic degradation which limits its application as an adsorbent. To overcome these drawbacks, the stability, solubility as well as adsorbing capacity can be enhanced through graft copolymerization reaction with vinyl monomers to develop hybrid material with good physico-chemical properties. Graft copolymers of acrylate monomers onto sodium alginate could be used as an alternative cheap adsorbent for heavy metal removal in wastewater treatment processes due to their origin from unlimited resources and availability of various functional groups [10]. Alginate has proved to be effective metal chelator [11], because it can act as a polyhydroxy or polycarboxylic acid chelating agent or can act as both. In the present work, graft copolymerization of methyl methacrylate (MMA) onto sodium alginate using benzoyl peroxide initiator was carried out and grafting conditions were optimized.

MATERIALS AND METHODS

Sodium alginate, methyl methacrylate (MMA), benzoyl peroxide (BPO) were purchased from Sigma-Aldrich (USA), MMA monomer was distilled under reduced pressure prior to use. BPO was further purified by dissolving in chloroform and precipitate in excess methanol. Methanol and acetone from QRëc (Selangor, Malaysia). All other chemical reagents were analytical grade and used as received.

Experimental

Graft copolymerization

The grafting reactions were carried out under nitrogen atmosphere in a 250 mL three-necked flask equipped with a reflux condenser and a magnetic bar stirrer, immersed into oil bath. Nitrogen gas was purge into the flask to remove oxygen during the reaction. Known amount of sodium alginate was added into the reaction flask containing distilled water (100 mL). After sodium alginate was completely dissolved, the required amount of BPO dissolved in 3 mL of acetone was added slowly to the reaction flask. The mixture was stirred for 20 min., and the required amount of MMA monomer was added. After the reaction time was over, the slurry was poured into methanol to induced precipitation. The precipitate was filtered, washed with acetone, dried in a vacuum oven at 60 °C until a constant weight and kept in a desiccator. The graft copolymer samples thus obtained were extracted for 24 h using acetone by Soxhlet extraction to remove the poly(methyl methacrylate) homopolymer. Finally the graft copolymer samples (NaAlg-*g*-PMMA) were oven dried at 60 °C to constant weight.

The grafting percentage G (%) and yield of graft copolymerization were calculated using Equation (1) & (2), respectively, [12-13].

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

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

where W_1 is the initial weight of sodium alginate, W_2 is the weight of the graft copolymer after Soxhlet extraction and W_3 is the weight of methyl methacrylate.

Characterization

The graft copolymers were characterized using the following techniques namely, FTIR analysis (Frontier, Perkin Elmer), thermogravimetric analysis (TA Q500 Thermal Instrument), scanning electron microscope (JEOL JSM 6390LV) and Solid-state ^{13}C-NMR spectra were recorded on Bruker Avance III HD spectrometer.

RESULTS AND DISCUSSION

Effect of reaction temperature

Reaction temperature is very important parameters that affect graft copolymerization. The effect of reaction temperature was investigated at different temperatures ranging from 60°C to 90°C while keeping other variables constant. The results obtained (Table 1) showed that graft copolymerization was favored at a relatively high temperature of 80°C, where percentage grafting of 78.90% and grafting yield of 19.72% were achieved under this temperature. High temperature promotes decomposition of BPO which produce free radicals resulting in increasing polymer macroradicals concentrations, as well as diffusion rate of the methyl methacrylate monomer in close medium of sodium alginate, thus enhances the graft copolymerization. However, with further increase in temperature (90°C), the percentage grafting was decreased due to the increase in conversion of initiator to free radicals which would promote early termination of the growing radicals.

Table 1: Effect of temperature on G (%) and Y (%) of NaAlg-*g*-PMMA

Temperature (°C)	G (%)	Y (%)
60	18.30	4.57
70	33.30	8.32
80	78.90	19.72
90	63.20	15.80

Grafting conditions: [MMA] = 3.99×10^{-1} M, [BPO] = 2.06×10^{-3} M, [Alg] = 1%, w/v, and reaction time = 1 h.

Effects of monomer concentration on preparation of NaAlg-*g*-PMMA

Reactivity and concentration of monomer has great role in graft copolymerization. Table 2 shows the influence of MMA concentration on percentage grafting G (%) and grafting yield Y (%). It can be seen from this table that in the beginning G (%) as well as Y (%) increased rapidly with increasing monomer concentration up to 7.99×10^{-1} M. The increase in percentage of grafting is probably due to the increase in the diffusion rate of the monomer which provides more opportunity for grafting. Besides this, gel effect (solubility of PMMA in its own monomer) can inhibit termination of growing polymer chains. The decrease in percentage grafting observed beyond optimum amount may be due to the increase in homopolymerization. It is commonly reported that the percentage grafting increases with monomer concentration up to a certain point and then decreases with further increase in monomer concentration [14-16]. This behavior showed that the initial increase in monomer concentrationin close vicinity to the backbone enhanced grafting. Beyond the optimum concentration, the increase in monomer concentration promoted the homopolymerization reactions.

Table 2: Effect of amount monomer on G (%) and Y (%) of Alg-*g*-PMMA

[MMA] $\times 10^{-1}$ M	G (%)	Y (%)
2.99	28.10	14.05
3.99	78.90	19.20
5.99	142.00	23.67
7.99	168.00	21.00
9.99	154.20	15.42

Grafting conditions: Temp. = 80°C, [BPO] =2.06×10^{-3} M, [NaAlg] = 1 %, w/v, and reaction time = 1 h.

Effect of initiator concentration on preparation of NaAlg-*g*-PMMA

The nature of initiator, concentration as well as solubility has great effect on grafting. In fact, the grafting rate is dependent upon amount initiator, monomer and the backbone. The results (Table 3) showed that both G (%) and Y (%) increased with increasing BPO content from 2.06×10^{-3} to 10.32×10^{-3} M, and then decreased thereafter. Relatively high concentration of BPO resulted in a reduction of grafting due to generation of more initiating radicals which could lead to early termination prior to monomer addition as well as termination of growing polymer, consequently, lowering G (%) and Y (%). Similar observation has been reported by other researchers [17].

Table 3: Effect of amount of initiator on G (%) and Y (%) of NaAlg-*g*-PMMA

[BPO] × 10^{-3} M	G (%)	Y (%)
2.06	124.10	15.51
4.13	202.20	25.27
6.19	158.00	19.75
8.26	122.30	15.28
10.32	93.00	11.62

Grafting conditions: Temp. = 80°C, [MMA] = 7.99 × 10^{-1} M, [NaAlg] = 1 %, w/v, and reaction time = 1 h.

Effect of sodium alginate concentration on preparation of NaAlg-*g*-PMMA

The amount of sodium alginate was varied in order to investigate its effect on the copolymerization while keeping other variables constant and the results are shown in Table 4. It was noted that the maximum percentage grafting was achieved when NaAlg (1%, w/v) was used. The lower percentage grafting observed at higher concentration of NaAlg may be attributed to high viscosities of the systems due to the gelling property of NaAlg. Therefore, it is difficult for the monomer molecules to diffuse effectively in the reaction system. Besides, high concentration of NaAlg can generate macroradicals which combine with each other to terminate the reaction.

Table 4: Effect of amount of NaAlg on G (%) and Y (%) of NaAlg-*g*-PMMA

Sodium alginate (%, w/v)	G (%)	Y (%)
0.5	72.00	9.00
1.00	202.20	25.27
1.50	176.00	14.70
2.00	147.00	14.33
2.50	89.00	11.12

Grafting conditions: Temp. = 80°C, [MMA] =7.99 × 10^{-1} M, [BPO] = 4.13 × 10^{-3} M, and reaction time = 1 h.

Effect of reaction time on preparation of NaAlg-*g*-PMMA

Effect of polymerization time was determined in the range of 1 to 5 h while keeping the other variables constant. After the predetermined reaction time was over, air was allowed to enter into the reaction flask to terminate the copolymerization and then by pouring the reaction mixture into cool methanol. Table 5 represents the influence of polymerization time on the grafting of MMA onto sodium alginate. It was observed that reaction time of 2 h yielded the highest G (%) (212%), beyond which it gradually decrease until leveled off. The high percentage of grafting is attributed by the increase in number of grafting sites in the initial stages of the reaction. The levelling of grafting with time could be due to the decrease in concentration of monomer as well as grafting sites due to the gel effect. It was observed that percentage grafting does appreciably change after optimum time is reached. Thus 2 h was chosen as the optimum duration for the grafting.

Table 5 Effect of reaction time on G (%) and Y (%) of Alg-*g*-PMMA

Time (h)	G (%)	Y (%)
1	202.20	25.27
2	212.00	26.50
3	211.10	26.38
4	191.00	23.87
5	191.00	23.87

Grafting conditions: Temp. = 80°C, [MMA] =7.99 × 10^{-1} M, [BPO] = 4.13 × 10^{-3} M, and [Alg] = 1 %, w/v.

Evidence of grafting by FTIR analysis

The FTIR analysis was carried out to ascertain the functional groups present in unmodified sodium alginate, the prepared graft copolymer (Alg-*g*-PMMA). The Spectrum of sodium alginate shown in Figure 1 revealed a broad absorption band at around 3446 cm^{-1} which is assigned to O–H stretching vibration. The peak observed at 1600, 1407 and 1028 cm^{-1} is due to stretching vibrations of COO^- (asymmetric), COO^- (symmetric) and C–O of glucopyronose ring respectively. The spectrum of the graft copolymer (Figure 2) indicates the presence of poly(methyl methacrylate) (PMMA) peaks with absorption bands at 2994 cm^{-1} assigned to C–H stretching. Meanwhile the peak at 1730 cm^{-1} indicates carbonyl ester stretching, the peak at 1145 cm^{-1} is assigned to –C–O–C– stretching and the peak at 749 cm^{-1} indicates deformation of $-CH_3$ group. The presence of these peaks in addition to those of sodium alginate provided substantial proved of grafting PMMA onto sodium alginate.

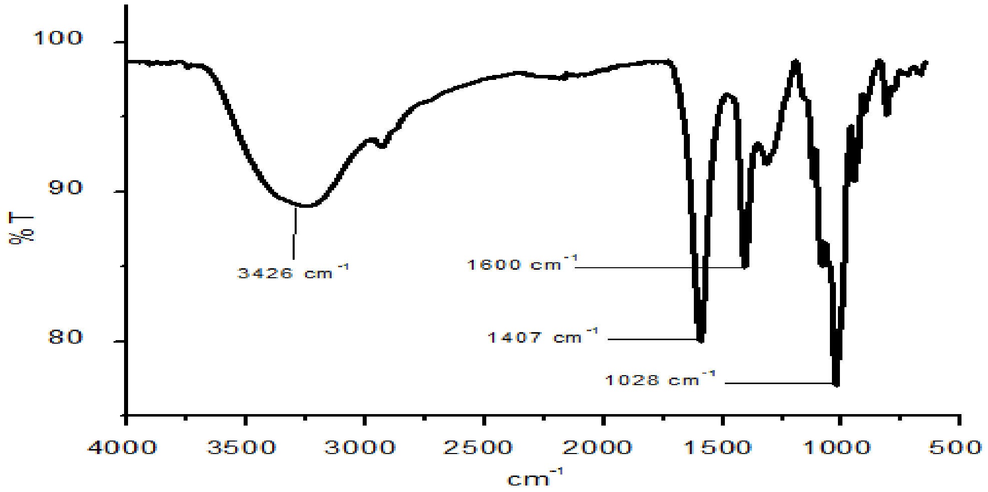


Figure 1: Infrared spectrum of sodium alginate

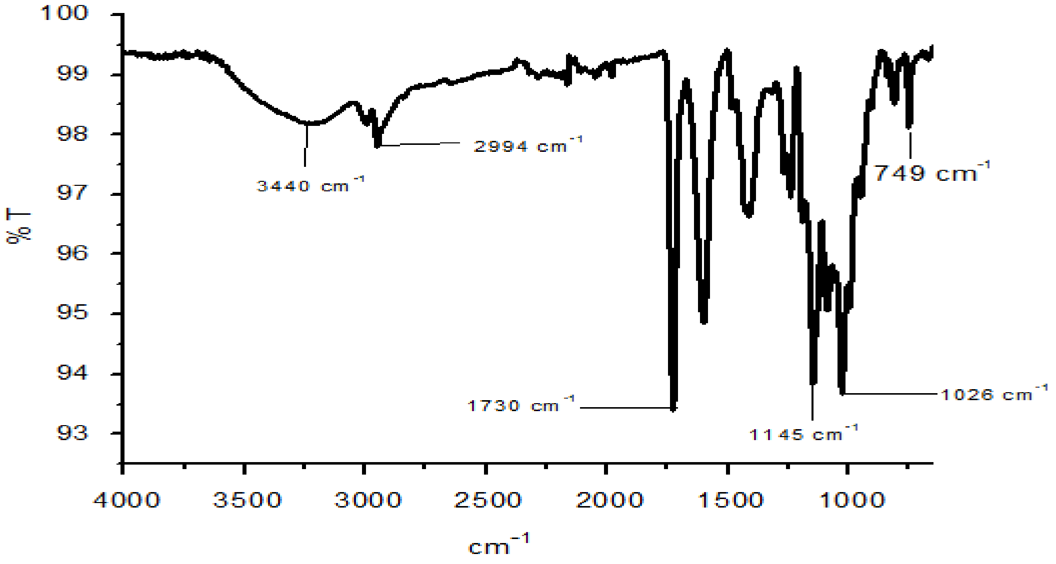


Figure 2: Infrared spectrum of graft copolymer (Alg-*g*-PMMA)

Thermogravimetric analysis (TGA)

The thermal properties of sodium alginate and the graft copolymer (Alg-*g*-PMMA) were investigated by thermogravimetric analysis. TGA thermogram of sodium alginate (Figure 3) showed two steps of weight loss. The initial weight loss of about 11.27% (0.873 mg) at 30-125°C was due to evaporation of moisture. The second weight loss of about 33.98% (2.632 mg) in the temperature range 200-250°C was due to complex processes that involve breakage of C–O–C glycosidic bond, carboxyl group (COO^-) with formation of water

(H_2O), methane (CH_4) and carbon dioxide (CO_2) as reported by other researchers [18]. The temperature at which 50% weight loss was found to be 270°C. However, in case of Alg-*g*-PMMA (Figure 4), three steps of weight loss was observed. The initial weight loss of about 21.54% (1.628 mg) in the temperature range of 200-250°C was due to degradation of of the NaAlg backbone with release of the gases. The second weight loss of about 38.50% (2.901 mg) in the temperature range of 300-430°C was due to degradation of PMMA chains. The final weight loss of about 7.25% (0.546 mg) in the range of 430-530°C was due to decomposition of the polymer backbone with ashes as residue. The temperature at which 50% weight loss was found to be 355°C which indicates that the thermal stability of the copolymer is higher than sodium alginate.

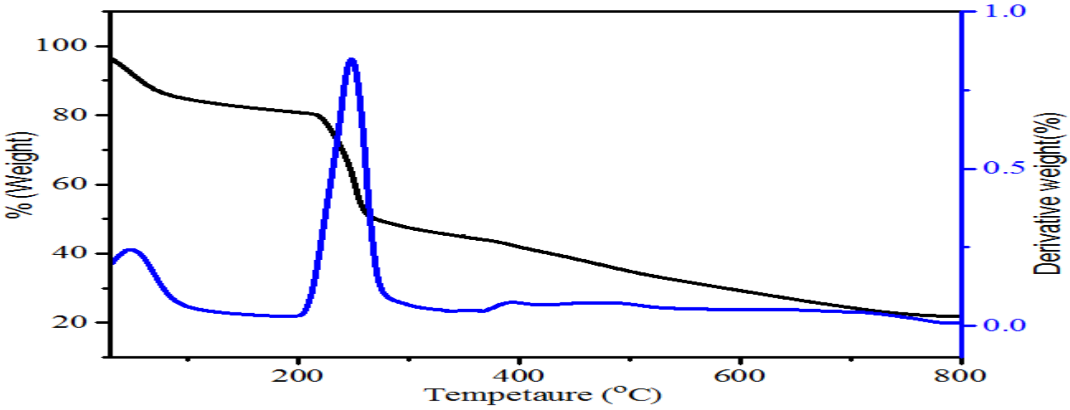


Figure 3: TGA thermogram of sodium alginate

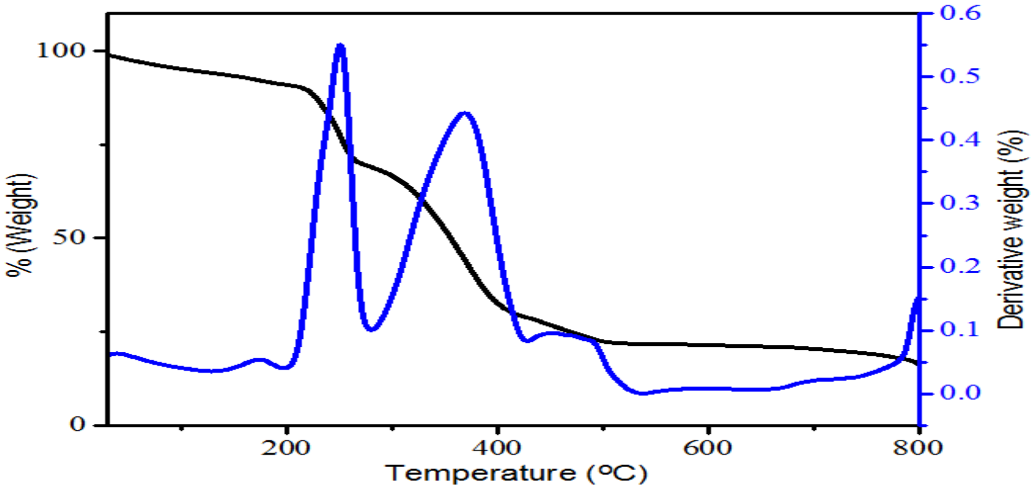


Figure 4: TGA thermogram of the graft copolymer (Alg-*g*-PMMA)

Solid-state ^{13}C-NMR analysis

The solid-state ^{13}C-NMR spectra of sodium alginate and the graft copolymer were well resolved using CP/MAS. The absorption peak at $\delta = 176.9$ ppm in the ^{13}C-NMR spectrum of sodium alginate Figure 5 (a) was assigned to the carboxyl carbon of COONa, the peak located at $\delta = 101.38$ ppm correspond to resonance of anomeric carbon. The peaks at $\delta = 67–80$ ppm were assigned to carbon atoms attached by –OH group of the pyranose ring. Meanwhile, the ^{13}C-NMR spectrum of Alg-*g*-PMMA Figure 5 (b) showed a resonance peak at $\delta =$ 176.9 ppm which was assigned to the carbonyl carbon. Similarly, the peaks at $\delta = 51.8$ ppm were assigned to the resonance of the carbon atom of methoxy group ($-OCH_3$) and methylene ($-CH_2-$) groups of PMMA. The resonance peak at $\delta = 45.1$ ppm was assigned to the quaternary carbon atom (>C<). The resonance peak at $\delta =$ 17.0 ppm was assigned to α-carbon atom of ($-CH_3$).

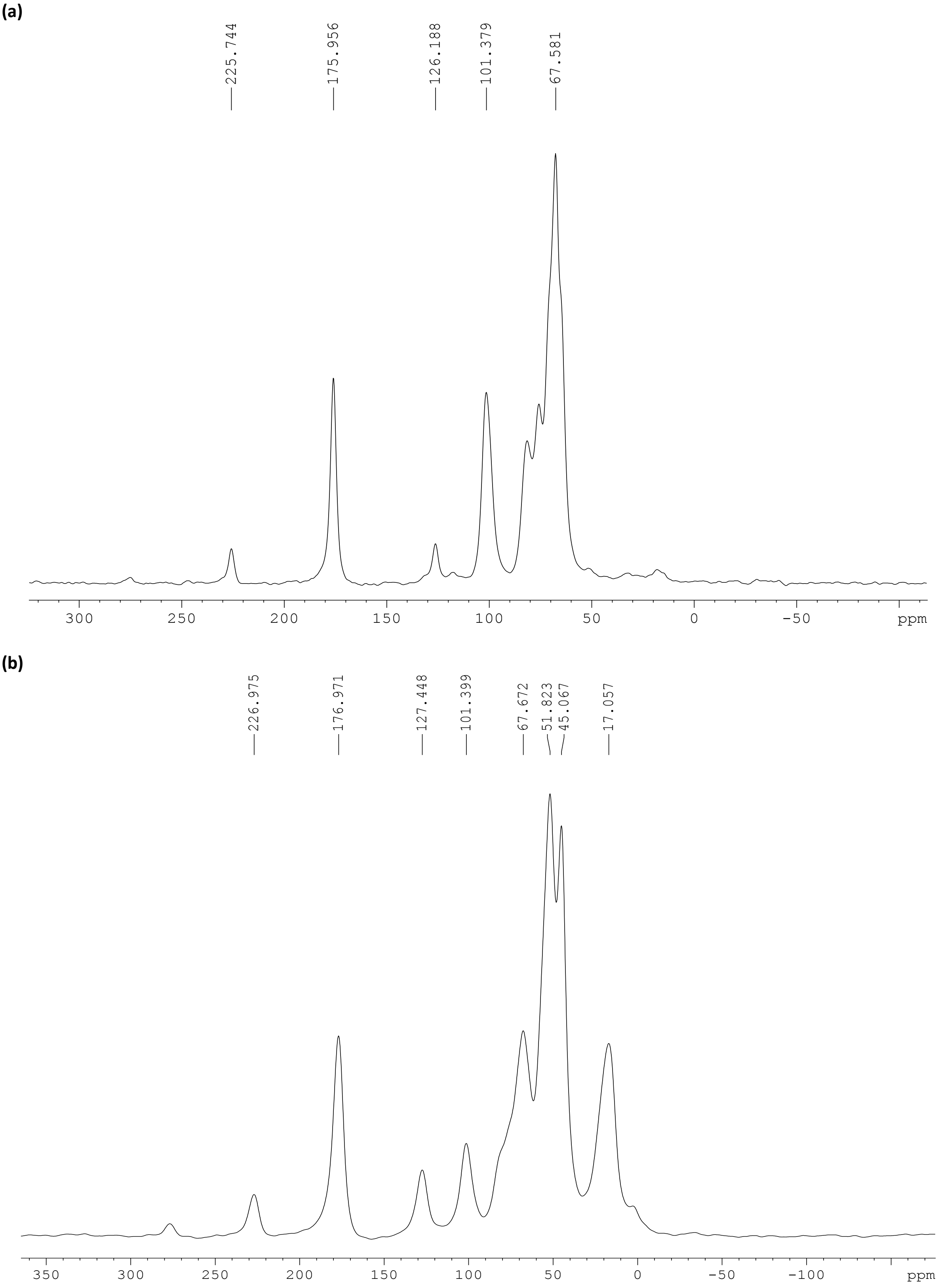


Figure 5: Solid-state ^{13}C-NMR spectra of (a) sodium alginate (b) Alg-*g*-PMMA copolymer.

Scanning electron microscopy analysis

Scanning electron microscopy (SEM) is a useful tool to evaluate the surface morphology of materials. The micrograph images of the unmodified sodium alginate and the graft copolymer after Soxhlet extraction

(Figure 6). It is obvious that the surface morphology of the graft copolymer after Soxhlet extraction disclose the surface porosity and texture of the material. This increase in texture and porosity of the graft copolymer could enhance adsorption property of the material

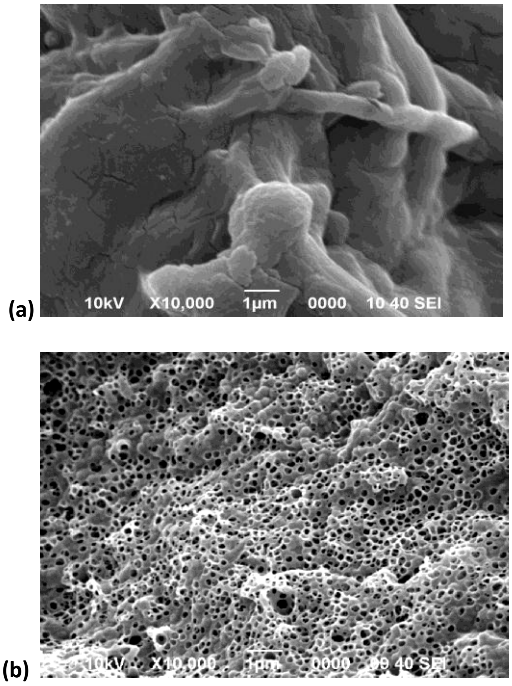
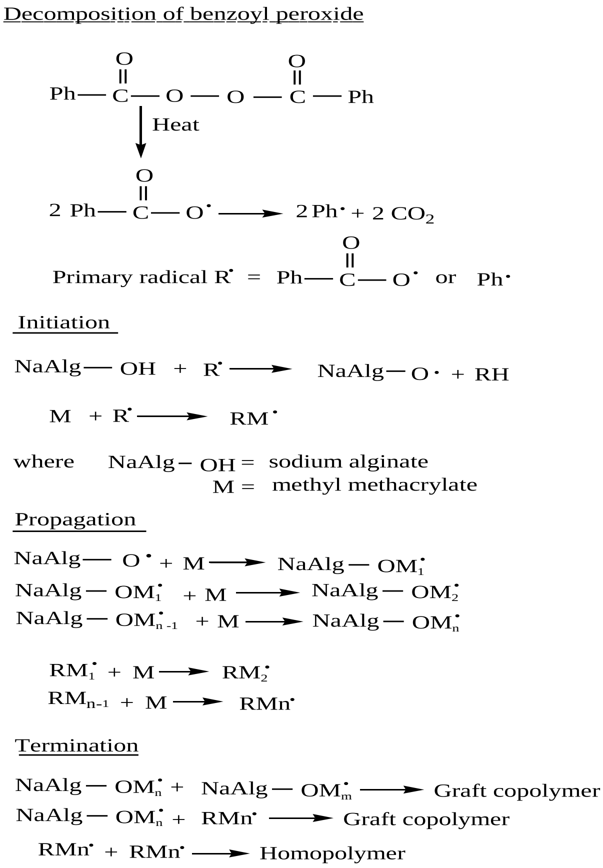


Figure 6: SEM micrographs (a) sodium alginate (b) graft copolymer (Alg-*g*-PMMA)


Decomposition of benzoyl peroxide

$$\mathrm{Ph-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-Ph}\ \xrightarrow{\text{Heat}}\ \mathrm{2\ Ph-\overset{\overset{O}{\|}}{C}-O^{\bullet}} \longrightarrow \mathrm{2\,Ph^{\bullet} + 2\ CO_2}$$

$$\text{Primary radical } \mathrm{R^{\bullet}} = \mathrm{Ph-\overset{\overset{O}{\|}}{C}-O^{\bullet}} \text{ or } \mathrm{Ph^{\bullet}}$$

Initiation

$$\mathrm{NaAlg-OH + R^{\bullet} \longrightarrow NaAlg-O^{\bullet} + RH}$$

$$\mathrm{M + R^{\bullet} \longrightarrow RM^{\bullet}}$$

where $\mathrm{NaAlg-OH}$ = sodium alginate
M = methyl methacrylate

Propagation

$$\mathrm{NaAlg-O^{\bullet} + M \longrightarrow NaAlg-OM_1^{\bullet}}$$
$$\mathrm{NaAlg-OM_1^{\bullet} + M \longrightarrow NaAlg-OM_2^{\bullet}}$$
$$\mathrm{NaAlg-OM_{n-1}^{\bullet} + M \longrightarrow NaAlg-OM_n^{\bullet}}$$

$$\mathrm{RM_1^{\bullet} + M \longrightarrow RM_2^{\bullet}}$$
$$\mathrm{RM_{n-1} + M \longrightarrow RMn^{\bullet}}$$

Termination

$$\mathrm{NaAlg-OM_n^{\bullet} + NaAlg-OM_m^{\bullet} \longrightarrow \text{Graft copolymer}}$$
$$\mathrm{NaAlg-OM_n^{\bullet} + RMn^{\bullet} \longrightarrow \text{Graft copolymer}}$$
$$\mathrm{RMn^{\bullet} + RMn^{\bullet} \longrightarrow \text{Homopolymer}}$$

Scheme 1: Plausible mechanism for the graft copolymer formation

A plausible general mechanism of grafting methyl methacrylate onto sodium alginate initiated by benzoyl peroxide is shown in Scheme 1. The first stage is the decomposition of initiator. It is well known that BPO decomposes under suitable temperature to form pair of free radicals (2 $PhCOO^{\bullet}$) by the cleavage of oxygen-oxygen bond and further decomposition yields phenyl radicals (2 $Ph^{\bullet}$) and carbon dioxide (CO_2) gas. Some of these free radicals abstract hydrogen atom from the hydroxyl group on the sodium alginate molecules, thereby generating macroradicals ($NaAlg{-}O^{\bullet}$). The monomer molecules in the reaction medium in close vicinity of the active sites become acceptors of alginate radicals leading to chain initiation of the graft copolymer and subsequently become free radical donor to another neighboring monomer molecules. In this manner the propagation stage proceeds (chains growing). Propagation continued until termination occurred. One obvious termination mechanism occurred when two propagating radical chains coupled at their free radical ends. The other possible termination process may involve the combination of the grafted chains and the homopolymer chains to give graft copolymer product. In addition, two homopolymer chains can be terminated by coupling to each other to give homopolymer product.

Conclusion

The synthesis of poly(methyl methacrylate)-grafted-alginate has been carried out with methyl methacrylate and sodium alginate using benzoyl peroxide initiator. It was found that the optimum percentage grafting of 212% was achieved by varying the reaction conditions. The graft copolymers were characterized by using FTIR, TGA, SEM and ss^{13}C-NMR spectroscopy. Based on the results of TGA, thermal stability of the graft copolymer was higher in comparison of unmodified sodium alginate.

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References

[1] L Rahman, S Silong, Z Wan Md, M Zaki, M Ahmad. J Appl Polym Sci 2000; 76:516.
[2] A Bhattacharya, BN Misra. Prog Polym Sci 2004;29:767.
[3] KHM Mostafa. J Appl Polym Sci 1995;56:263.
[4] SN Bhattacharya, D Maldas. Prog Polym Sci 1984;10:171.
[5] SB Dash, AK Predhan, NC Pati, SL Nayak. J Macromol Sci Chem 1983;A19:343.
[6] MK Misra, BG Sar, G Norman. Polym Bull 1983;9:106.
[7] M Yadav, DK Mishra, A Sand. Carbohydr Polym 2011;84:83.
[8] P Rani S Mishra, G Sen. Carbohydr Polym 2013;91:686.
[9] AL Haug, S Olav. Acta Chemica Scand 1966;201:183.
[10] G Crini. Bioresource Technol 2006;97:1061.
[11] P Hyun Gyu, TW Kim, MY Chae, IK Yoo. Process Biochem 2007;42:1371.
[12] JS Shukla, SC Tewari, GK Sharma. J Appl Polym Sci 1987;34:191.
[13] K Kaewatatip, V Tanrattanakul. Carbohydr Polym 2008;73:647.
[14] SB Shah, CP Patel, HC Trevedi. Carbohydr Polym 1995;26:61.
[15] HL Young, JS Kim, HD Kim Key. Eng Mater 2005;279:450.
[16] M Sadeghi, G Nahid, S Fatemeh. J Sci Res 2011; 64: 587.
[17] I Nuran, K Fatma, I Murat. Carbohydr Polym 2010;79:665.
[18] I Nuran, K Fatma. Polym Bull 2013;70:1065.