

GRAFTING OF POLYACRYLONITRILE ONTO SODIUM ALGINATE USING BENZOYL PEROXIDE AS INITIATOR

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Abstract. In this study, grafting of polyacrylonitrile onto sodium alginate was carried out in aqueous medium using benzoyl peroxide (BPO) as initiator. The graft copolymers were characterized by Fourier transforms infrared spectroscopy, differential scanning calorimetry, thermogravimetric analysis, and scanning electron microscopy. The effects of reaction variables such as the ratio of monomer to sodium alginate, amount of BPO, reaction time and temperature on the percentage grafting G (%) were studied. The optimum conditions for grafting were achieved at a ratio of sodium alginate to acrylonitrile of 1:3 by weight, 0.1 g of BPO and reaction temperature and time of 80°C and 4 h, respectively. These conditions provided highest percentage of grafting and yield of graft copolymerization of 125.50% and 41.84%, respectively. The results indicate that benzoyl peroxide could be used as thermal initiator for grafting polyacrylonitrile onto sodium alginate

Keywords Grafting, sodium alginate, acrylonitrile, benzoyl peroxide, thermogravimetric analysis

1.0 INTRODUCTION

Modification of natural polymers (polysaccharides) by grafting vinyl monomers via radical polymerization mechanism has attracted the interest of many scientists[1]. This technique enables the synthesis of hybrid materials with broad applications than the unmodified natural polymers without damaging the initial properties of the substrate [2,3]. Among polysaccharides, alginate has important properties which rendered it a good material of choice for chemical modification because it possesses various functional groups together with unique physical properties such as gelling, thickening and swelling. These properties could be utilized in stabilization of suspensions, emulsions and film formation. Besides, alginate is non-toxic, renewable and biodegradable. Alginic acid or alginate (its salts or its derivatives) as shown in (Fig. 1) 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) arranged in an irregular blockwise pattern of varying proportions of GG, MG, and MM blocks[4-6]. Alginic acid is produced by brown algae species, the relative amounts of M and G, as well as their sequential arrangement along the polymer chain varies greatly with the source of the alginate, age of the algae, and the method of extraction [7]. Alginate has a broad range of applications in various fields such as in pharmaceutical for the controlled release of medicinal drugs[8], biomedical,[3,9] agriculture[10] and purification.[11-13]

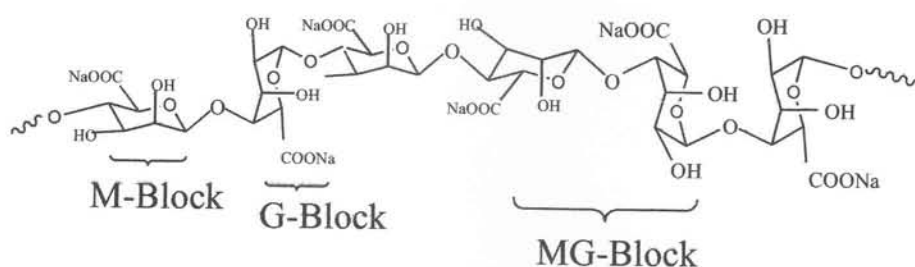


Figure 1:Block pattern of sodium alginate

From the literature survey, chemical modification of alginate by grafting polyacrylonitrile on its backbone using various redox initiating systems have been reported [14-17], no previous studies have been made on the graft copolymerization of acrylonitrile (AN) onto sodium alginate using benzoyl peroxide (BPO) as thermal initiator.

2.0 EXPERIMENTAL

2.1 Materials

Sodium alginate, benzoyl peroxide and acrylonitrile were from Sigma-Aldrich (Louis, USA), acrylonitrile monomer was distilled under reduced pressure before used in all the experiments. Dimethylformamide (DMF) and acetone from QRec (Selangor, Malaysia) were used as received.

2.2 Procedure for graft copolymerization

The grafting reactions were carried out under nitrogen atmosphere in a 250-mL three-necked flask equipped with a magnetic stirrer, and a nitrogen gas inlet system, immersed in a constant temperature bath. For each experiment, sodium alginate solution was prepared by slow addition of weighed amount of sodium alginate into 200 mL beaker containing distilled water (80g) and stirred vigorously using a glass rod until a viscous transparent solution was obtained. Then the solution was transfer into the reaction flask which was immersed into oil bath at reaction temperature, and then the required amount of BPO dissolved in acetone (5 mL) was added slowly to the slurry. After the mixture was stirred for 20 min the required amount acrylonitrile monomer was added. Graft copolymerization was carried out at various conditions. The graft copolymerization parameters include; alginate: acrylonitrile ratios 1:3, 1:1, 3:1 by weight, BPO content 0.05-0.5 g, reaction time 1-6 h and reaction temperature between (60-90°C). The nitrogen atmosphere and stirring were maintained throughout the experiment. After the reaction time was over, the slurry was poured into acetone. The product was filtered, dried in vacuum oven at 60°C to constant weight and kept in the desiccator

2.2.1 Separation of homopolymer

The products were washed using dimethylformamide (DMF) solvent by Soxhlet extraction for removing polyacrylonitrile homopolymer. The extraction was done for 24 h. After extraction the graft copolymer was dried in a vacuum oven at 60°C to constant weight and kept in the desiccator.

2.2.2 Estimation of grafting parameters

The graft copolymers were estimated by the following parameters; the percentage of grafting, G (%) and yield of graft copolymerization Y (%) from equation (1) and (2) respectively [18].

$$G (\%) = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

$$Y (\%) = \frac{W_1 - W_0}{W_2} \times 100 \quad (2)$$

where W_1 , W_0 , and W_2 denote, respectively, the weight of the grafted sodium alginate, the weight of the original sodium alginate and the weight of the monomer used.

2.2.3 Characterization of alginate-g-PAN

Fourier transform infra red spectroscopy (FTIR) was used to confirmed the grafting reaction. The dried samples were pressed under hydraulic pressure with KBr to form transparent discs. The spectra were taken using Perkin Elmer SpectrumTM 400 model (USA) and scanned at a frequency range of 4000 - 450 cm^{-1}

2.2.4 Thermal Analysis

2.2.4.1 Differential scanning Calorimetry

Differential scanning calorimetry (DSC) analysis was carried out using a Thermal Advantage Instrument (Q2000 TA Instruments, USA) using aluminum pan under a 50 mL/min nitrogen flow at the heating rate of 20°C/min on the second heating of a heating-cooling-heating cycle.

2.2.4.2 Thermogravimetric study

Thermogravimetric (TGA) study of sodium alginate and that of the Alg-g-PAN were carried out with a Thermal Analysis Instrument (Q500 TA, USA). The study was conducted in an inert atmosphere from 50°C to 800°C at a heating rate of 20°C/min.

2.2.5 Scanning electron microscopy analysis

The scanning electron microscopy (SEM) micrographs of pure sodium alginate and Alg-g-PAN before and after Soxhlet extraction were taken using a JEOL JSM 6390LVSEM (Tokyo, Japan). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold using auto fine coater (JFC-1600 model).

3.0 RESULTS AND DISCUSSION

In order to optimize the reactions conditions for grafting, the amount of initiator, monomer, sodium alginate as well as temperature and time were varied.

3.1 Effect of Sodium Alginate and Acrylonitrile ratio

Table 1 represents G (%) and Y (%) of various ratios of sodium alginate and acrylonitrile polymerized under various conditions. It was observed that in the system whereby sodium alginate acrylonitrile were varied, both values of G (%) and Y (%) show similar effects, in such a way that higher G (%) value showed higher Y (%). We found that the amount of sodium alginate and acrylonitrile ratios had great effects on percentage grafting G (%); the system with higher monomer concentration was more favorable. The highest acrylonitrile content (3g) gave the highest percentage grafting (125.50%). Therefore as the amount of acrylonitrile content increases, the diffusion of the monomer increases into the sodium alginate backbone this provides more opportunity for graft copolymerization and consequently percentage grafting increases. This is in agreement with the results obtained in graft copolymerization of acrylonitrile onto sodium alginate initiated by hydrogen peroxide[14]. In the ratio sodium alginate: acrylonitrile (3:1), it was observed that both grafting percentage G (%) and, yield of graft copolymerization Y (%) were small values. Because the viscosities of the systems increased with increase amount of alginate, therefore it is difficult for monomer molecules to diffuse effectively; as a result fewer reactive sites were generated.

3.1.1 Effect of Temperature

The influence of temperature on the grafting was investigated by carrying out the reaction at different temperatures in the range 60-90°C and keeping the other variables constant. In Table 1, the G (%) increased up to 125.50 % at temperature of 80°C then decreased at 90°C. The temperature enhances the activation of macroradicals as well as diffusion of the monomer. It was observed that further increase in temperature to 90°C led to a decrease of G (%), which can be attributed to the increase in the formation of homopolymer as well as premature termination of the active sites and increases the contribution of chain transfer reaction. Besides, at the reaction temperature of 60°C graft copolymerization did not occur. Although, every polymerization reaction has its own optimum reaction temperature, similar behavior was observed in the case of grafting itaconic acid onto sodium alginate using BPO as initiator[19].

Table 1
 Effect of polymerization parameters on the percentage grafting, G (%) and Y (%)

Alginate (g) W_0	AN (g) W_2	Temp (°C)	W_1 (g) ^a	G (%) ^b	Y (%) ^c
1	3	60	-	-	-
1	3	70	1.47	47.00	15.67
1	3	80	2.25	125.50	41.84
1	3	90	1.51	51.00	17.00
1	1	60	-	-	-
1	1	70	1.03	3.00	3.00
1	1	80	1.31	31.00	31.00
1	1	90	1.26	26.00	26.00
3	1	60	-	-	-
3	1	70	3.01	0.33	1.00
3	1	80	3.18	6.00	18.00
3	1	90	3.13	4.33	13.00

Reaction conditions: Time = 4 h, water = 80 g and BPO = 0.1 g
 W_0 represents weight of sodium alginate
^a W_1 represents weight of the copolymer after Soxhlet extraction
 W_2 represents weight of acrylonitrile
^b G (%) represents percentage grafting
^c Y (%) represents percentage yield

3.2 Effect of Amount of Benzoyl Peroxide

The effect of amount of benzoyl peroxide (0.05- 0.4 g) on percentage grafting is shown in Fig. 2. Percentage grafting increases from (0.05- 0.1 g), this could be due to the formation of a greater number of grafting sites as a result of abstraction of hydrogen atom from the sodium alginate backbone. However, increasing the amount of BPO beyond 0.1 g resulted in decreased in percentage grafting due to the increase of termination reactions. Therefore, the optimum amount of BPO for grafting acrylonitrile onto sodium alginate was found to be 0.1 g.

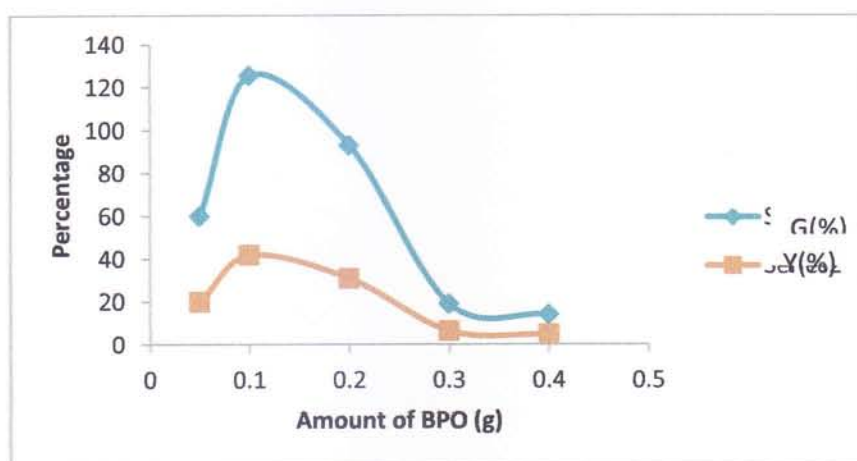


Figure 2: Effect of amount of BPO. Reaction conditions: Alginate = 1 g, AN = 3 g, water = 80 g, reaction time = 4 h, Temp = 80°C

3.3 Effect of Reaction Time

The reaction time plays a significant role in the graft copolymerization. The effect of reaction time was determined in the range (1-6 h) keeping the other variables constant and the results are shown in Fig.3. It was observed that grafting percentage G (%) and yield of graft copolymerization Y (%) increased steadily with the increase of polymerization time up to 4 h. The highest percentage of

grafting G (%), 125.50% was achieved at that time. Further increase of time beyond 4 h, both G (%) and Y (%) began to decrease. This was due to the decrease in monomer concentration and initiator concentration and possibly the reduction of grafting sites on the sodium alginate backbone. However, graft copolymerization did not occur at polymerization time of 1 h.

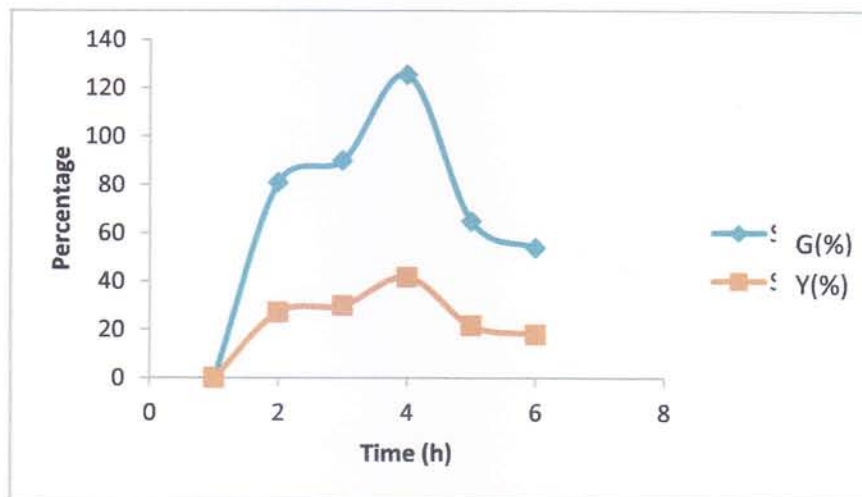


Figure 3: Effect of reaction time. Reaction conditions: Alginate = 1 g, AN = 3 g, BPO = 0.1 g, water = 80 g, Temp = 80°C

3.4 Evidence of grafting

3.4.1 IR Spectroscopy

Fig. 4 shows the FT-IR spectra of sodium alginate and Alg-g-PAN. In case of sodium alginate (Fig.4a). The broad peak at 3421cm^{-1} correspond to OH groups, peaks at around 2936 , 1619 , and 1416cm^{-1} , indicating the stretching vibrations of aliphatic C—H, COO^- (asymmetric), COO^- (symmetric), and C—O respectively. Moreover, a new absorption band in the spectrum of Alg-g-PAN (Fig. 4b) at around 2243cm^{-1} characteristics of nitrile group appeared which was not present in the sodium alginate spectrum.

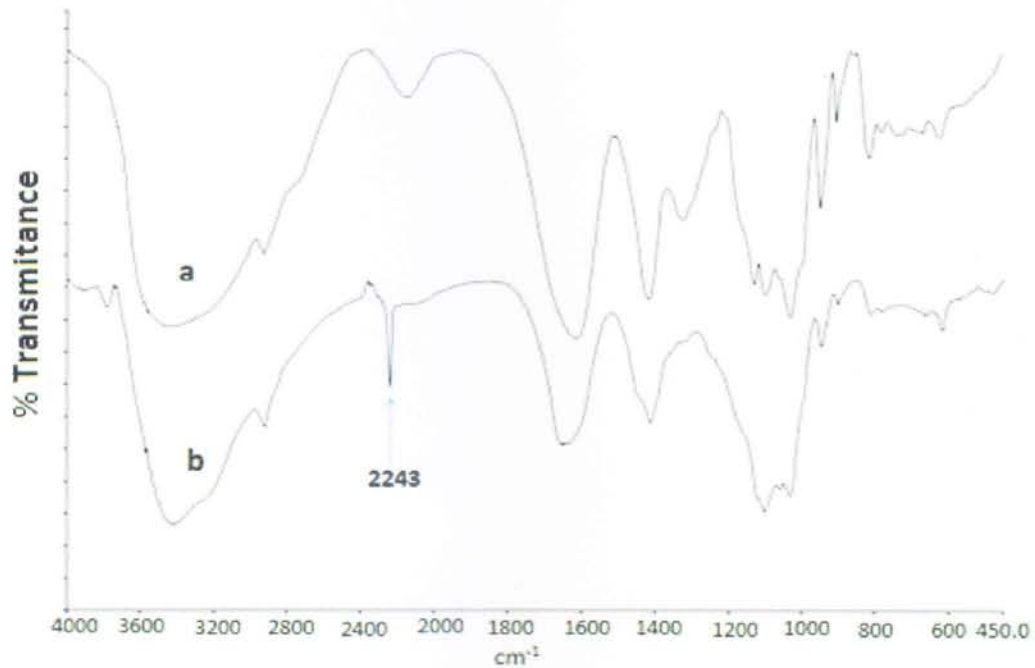


Figure 4: Infrared spectra of sodium alginate (a) and Alg-g-PAN (b)

3.4.2 Thermal Analysis

3.4.2.1 Differential Scanning Calorimetry

DSC thermogram of pure sodium alginate is displayed in Fig. 5, and no glass transition temperature (T_g) was observed after heating-cooling-heating cycle. In case of Alg-g-PAN (Fig. 6), T_g of polyacrylonitrile chains grafted was found to be 127°C higher than normal polyacrylonitrile.

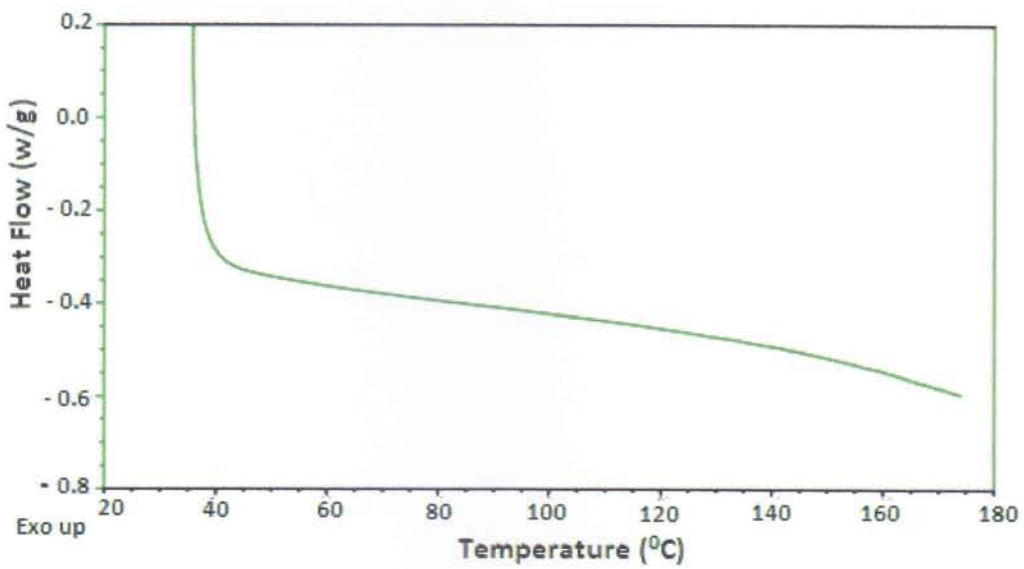


Figure 5: DSC thermogram of sodium alginate

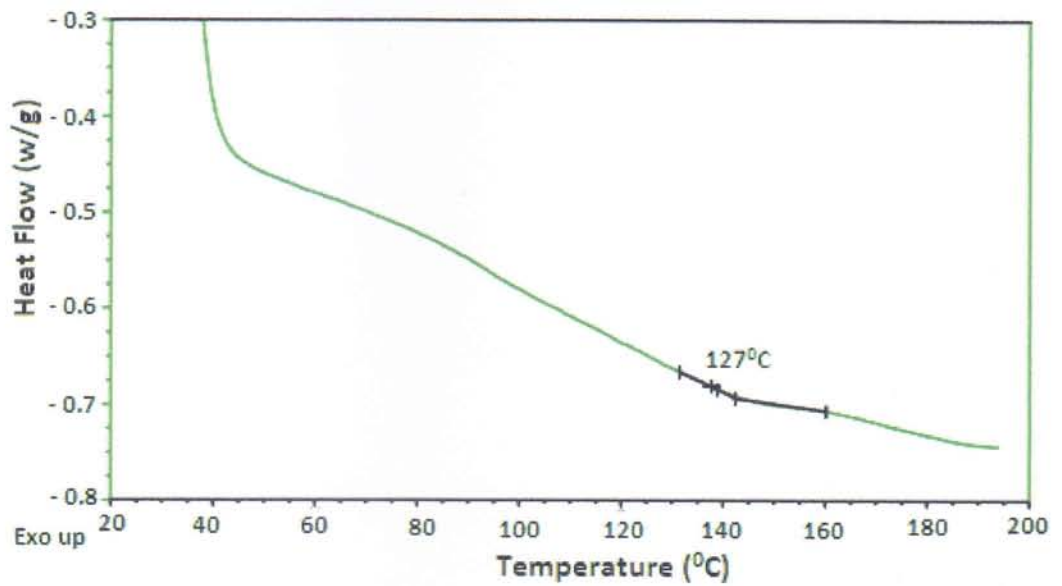


Figure 6: DSC thermogram of Alg-g-PAN

3.4.2.2 Thermogravimetry study

Thermogravimetric analysis (TGA) of sodium alginate is shown in Fig.7. It was observed that sodium alginate showed a weight loss in three steps. The initial weight loss of about 14.67% at 50- 125°C, could be due to evaporation of water as has been reported by others [20]. The second step (200-250°C) was due to degradation of carboxylate group (COO⁻) which resulted in the loss of CO₂ (decarboxylation) with mass loss of about 37.70%. Total decomposition of alginate backbone was observed at the temperature above 400°C.

However, in case of Alg-g-PAN (Fig.8) different thermal behavior was observed. The first stage of weight loss of about (18.78%) starts from 200 - 250°C, was due to degradation of carboxylate group (COO⁻) to release CO₂. The second stage of weight loss (26.33%) started at 320°C -550°C this could be due to degradation of polyacrylonitrile chains grafted. The third stage of weight loss from 550 - 800°C was due to decomposition of sodium alginate backbone. The behavior of weight loss in decarboxylation process reveals that the graft copolymer had lower weight loss than sodium alginate, because of polyacrylonitrile chains grafted. This suggests that the thermal stability of sodium alginate has been improved.

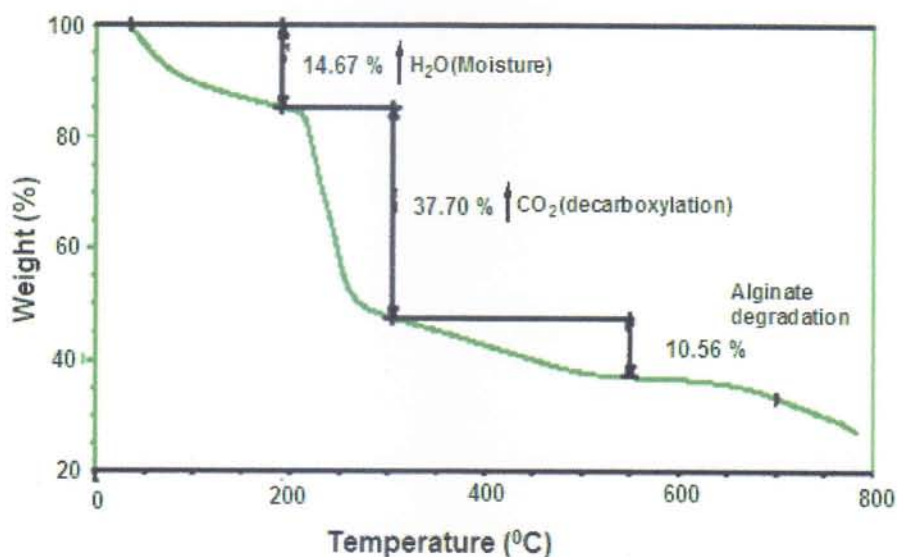


Figure 7: TGA thermogram of sodium alginate

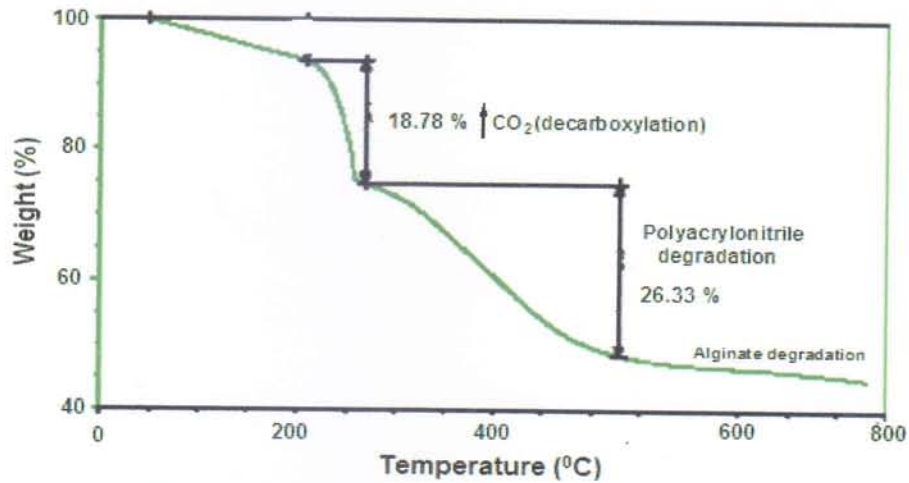


Figure 8: TGA thermogram of Alg-g-PAN

3.5 Scanning electron microscopy (SEM) analysis

SEM micrographs of the graft copolymer before and after soxhlet extraction are shown in Fig 9(a) and 9(b) respectively. It was obvious that the surface morphology of the graft copolymer had rough surface. However, after soxhlet extraction such rough surface disappeared and sponge-like structure appeared due to grafting of polyacrylonitrile onto sodium alginate.

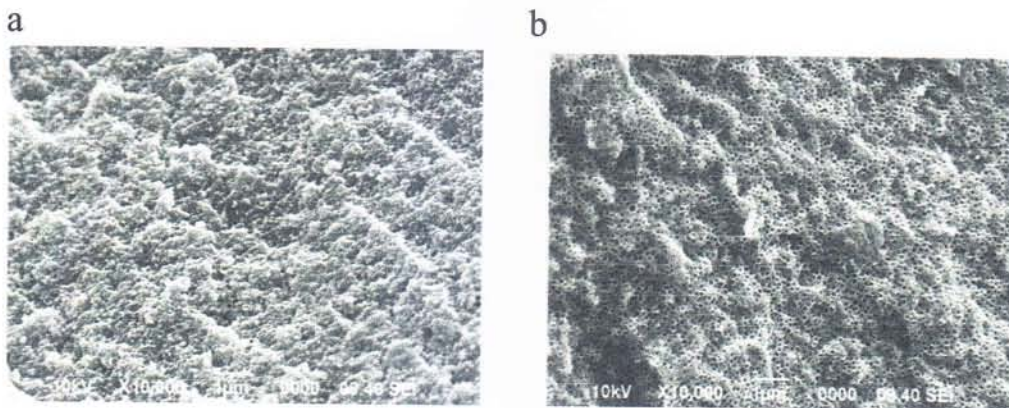


Figure 9: SEM micrographs of Alg-g-PAN (a) before soxhlet extraction and after soxhlet extraction (b)

4.0 CONCLUSIONS

Modification of polysaccharides by graft copolymerization reaction particularly employing free radicals to initiate the reaction is an important technique to obtain a chemically modified material with enhanced properties. The graft copolymerization of polyacrylonitrile onto sodium alginate was carried out using benzoyl peroxide as initiator. The optimum reaction conditions were found to be; BPO 0.1 g, (1: 3 by weight) sodium alginate to acrylonitrile ratio, reaction temperature and time of 80°C and 4 h. Under the optimized conditions the percentage grafting G (%) and yield of graft copolymerization were 125.50% and 41.84% respectively. The evidence obtained from infrared spectroscopy, thermogravimetric analysis and scanning electron microscopy have proven the grafting of sodium alginate with polyacrylonitrile. Based on thermogravimetric analysis result, we found that the stability of sodium alginate has improved greatly.

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