PREPARATION AND EVALUATION OF GRAFT COPOLYMER BASED ON SHRIMP CHITIN AND ACRYLONITRILE FOR WASTE WATER TREATMENT

1. Graft Copolymerisation of Acrylonitrile onto Chitin

Pham Thi Bich Hanh

Institute of Chemistry - National Centre for Natural Science and Technology

A graft material based on shrimp chitin (chitin from shrimp shell) and acrylonitrile (AN) has been successfully prepared in an aqueous suspension using chitin thiocarbonate-Fe(II)-hydrogen peroxide redox system as an initiator. The optimum conditions for graft copolymerization of AN onto chitin were investigated by observing the effect of ferrous ammonium sulfate (FAS), hydrogen peroxide and monomer concentrations as well as pH of polymerization solution, reaction time and reaction temperature on the graft yield. The graft copolymer was characterized by Fourier transform-infrared spectroscopy and thermal analysis (TGA and DSC).

INTRODUCTION

Chitin is an abundant biopolymer like cellulose and is distributed in the shell of crustacean, e.g. crab and shrimp, and the cuticle of insects and also in the cell wall of some fungi and microorganisms. Chitin consists of 2-acetamido-2-deoxy-(1-4)-β-D-glucopyranose residues (N-acetyl-D-glucosamine units) which has intra- and inter-molecular hydrogen bonds and is water-insoluble due to its rigid crystalline structure [1].
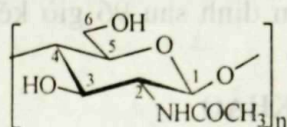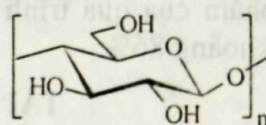
Chitin   Cellulose

Although chitin is an abundant biomass resource whose annual production is close to that of cellulose, the insolubility in common organic solvents has delayed its utilization and basic research. Chemical modification of this rigid aminopolysaccharide should lead to an interesting novel type of polymeric material. Our current interest has focused on various modes of chemical modifications. Graft copolymerisation onto chitin is one of the most attractive modifications in many respects. It is expected to make possible a wide variety of transformations. Whereas graft copolymerization onto cellulose has been studied extensively, that onto chitin or chitosan has been explored only recently [2]. Some initiation methods for graft copolymerization of vinyl monomers onto chitin have been reported, such as, γ-ray [3], UV [4], Ce(IV) [5,6,7,8,9], chitin thiocarbonate-Fe(II)-H_2O_2 [10]. These graft copolymers are of importance in view of new industrial application such as water absorbents, ion exchangers, flocculants, membranes, modified electrodes and, principally, chelating agents [9]. This work reports the heterogeneous reaction grafting of acrylonitrile (AN) onto shrimp chitin (α-chitin) powder using chitin thiocarbonate-Fe(II)-H_2O_2 redox system.

EXPERIMENTAL

Materials and reagents

α-Chitin was extracted from shrimp shell, by modified Hackman method [11], dried *in vacuo* at 60°C, purified by extracting with methanol [12] and powdered to a 50 mesh size before use. The degree of deacetylation (DA) found by elemental analysis [13] was about 0.15. Acrylonitrle (AN) (reagent grade, China) was purified by distillation under reduced pressure before use. All other commercial available chemicals were analytical grade.

Thiocarbonation of chitin powder[10]

The chitin sample was placed in stoppered glass vessel containing the thiocarbonation solution (1% NaOH, w/v; 1% CS_2 v/v). The material-to-liquor ratio was 1:50, and the temperature of solution was kept at 40°C. The contents of the vessel were stirred continuously by magnetic stirrer through the thiocarbonation reaction. After 4h, the solution was drained and the powder thoroughly washed with distilled water until the pH of the washing liquor was 7. The chitin after thiocarbonation reaction will be referred to as chitin thiocarbonate.

Graft procedure [10]

The chitin thiocarbonate was pretreated by immersing in FAS solution kept at 40°C for 30 minutes with continuous stirring by magnetic stirrer. After impregnation, the sample was washed repeatedly with distilled water and filtered to remove the unadsorbed ferrous ions from the sample surface before introducing into the polymerization solution. The sample was placed in a glass vessel containing the grafting solution, which consisted of known concentrations of hydrogen peroxide and monomer at the chosen pH. The material-to-liquor ratio was 1:30. The contents of the reaction vessel, throughout the reaction period, were stirred continuously to shun the precipitation and the heaping up of the homopolymer all over the sample surface. After the specified time intervals, the reaction was arrested by quenching with ice-cold water. The homopolymer along with the grafted chitin were filtered off and washed with distilled water. The homopolymer of acrylonitrile was extracted with water using the Soxhlet apparatus and then dried at 80°C. The obtained product was considered to be the graft copolymer (ChAN). Homopolymer was extracted thoroughly with dimethyl formamide for polyacrylonitrile (PAN).

The graft yield (GY) was calculated as follows: $\quad GY (\%) = \dfrac{w_1 - w_o}{w_o} \times 100$

where w_o and w_1 denote the weights of original sample (chitin) and grafted sample (ChAN), respectively.

Characterization

Infrared (IR) spectra were recorded on IMPACT-410 Fourier-transform IR (FTIR) spectrometer (Germany) with the potassium bromide technique. Thermal analysis (TGA and DSC) of all the samples were carried out on TA-50 thermal analyzer (Shimadzu). Both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the samples were performed up to a temperature of 700°C, starting from room temperature in an atmosphere of nitrogen with flow rate 20mL/min. The heating rate was 10°C/min in all cases.

RESULTS AND DISCUSSION

Graft Copolymerisation

The reaction mechanism of graft copolymerization of vinyl monomers onto chitin using the chitin thiocarbonate-Fe(II)-H_2O_2 redox system as an initiator was shown[10]. Effect of the variation of any factor on the graft yield was evaluated by keeping all other conditions constant. The results showing the effects of ferrous ions and hydrogen peroxide concentrations as well as pH of polymerization solution on the graft yield are shown in Table 1. It is observed that Fe^{2+} concentration increased the graft yield until the concentration of Fe^{2+} reached 0.15%; and it had adverse effects when the concentration of Fe^{2+} was higher than 0.15%. The increase of GY could be due to the creation of OH free radical species and the decrease of GY could be due to the consumption of OH free radical during graft copolymerization. As shown in Table 1, the data indicate that the graft yield slightly increases until the concentration of hydrogen peroxide reaches to 0.3%, then decreases thereafter. The decrease of graft yield above 0.3% H_2O_2 was explained in a view of the radical termination. Namely, a lot of free radicals formed above the concentration between growing chains and oligomeric vinyl radicals [10]. Table 1 also shows the effect of pH of polymerization solution on the graft yield that was determined by calculating the increase of sample weight. Obviously, the graft yield increased with increasing pH, attaining a maximum at pH 3, decreasing at higher pH. This could be explained in terms of an accelerated oxidation/reduction reaction at lower pH. At the same time the fast disintegration and oxidation processes of chitin-thiocarbonate lead to the destruction of the OH free radical by ferrous ions.

Table 1. Effect of reaction conditions on the graft yield of ChAN.

Reaction conditions		Graft yield (%)	Remarks
$[Fe^{2+}]$	0	21.2	
(g/100mL)	0.05	60.3	$[H_2O_2]=0.3\%$
	0.1	79.5	pH = 3
	0.15	82.6	
	0.2	78.4	
$[H_2O_2]$	0 (%)	0	
	0.1	80.3	$[Fe^{2+}] = 0.15$
	0.2	81.5	(g/100mL)
	0.3	82.4	pH = 3
	0.4	73.5	
pH	1	42.1	
	2	64.5	$[H_2O_2]=0.3\%$
	3	83.2	$[Fe^{2+}] =$
	4	59.4	0.15(g/100mL)
	5	32.9	

Conditions: Chitin, 1g; AN, 2g; time, 90 min.; temperature, 60°C.

The effects of the variation of reaction time, reaction temperature and monomer concentration on the graft yield of copolymerization AN onto chitin are shown in Table 2.

Acrylonitrile (g)	Temperature (°C)	Time (min.)	Graft yield (%)
1	60	120	41.9
2	60	120	87.5
3	60	120	92.4
4	60	120	99.5
5	60	120	105.3
2	40	120	35.8
2	50	120	48.6
2	60	120	99.2
2	70	120	98.5
2	60	30	40.3
2	60	60	75.6
2	60	90	83.1
2	60	120	99.8
2	60	150	99.5

Conditions: chitin, 1g; [H_2O_2], 0.3%; pH, 3; [Fe^{2+}], 0.15(g/100mL).

As shown in Table 2, the increase of the monomer led to an increase of the graft yield. The significant increment in the graft yield by increasing monomer concentration could be attributed to the greater availability of monomer molecules in the vicinity of the chitin at a higher monomer concentration. It is apparent from Table 2 that the graft yield increased with increasing reaction temperature, showing a maximum value at 60°C, then decreased. This could be explained that the radicals initiate the homopolymerization rather than the graft copolymerization at higher temperatures (>60°C). Table 2 also shows the effect of reaction time on the graft yield. It is clear that the graft yield increased with increasing reaction time, attaining a maximum after 120 minutes, then leveled off. Leveling off could be attributed to a drop of monomer and initiator concentrations as well as to a decrease of the available active grafting sites on the chitin backbone [10].
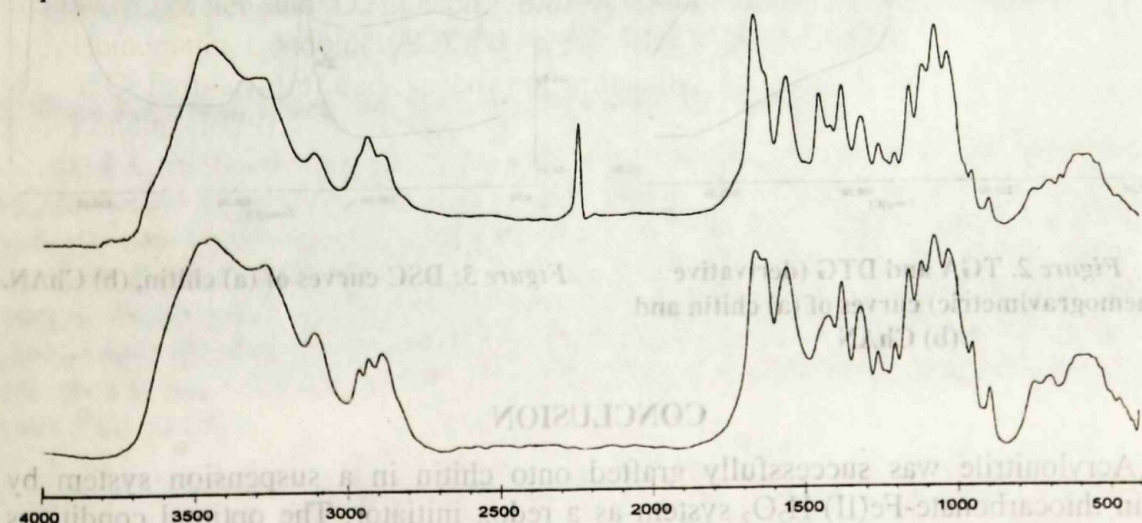
Characterization

IR spectra

Figure 1. IR spectra of chitin (a- below), ChAN (b- upper).

To confirm the changes in chemical structure of the chitin after grafting, FTIR spectroscopy measurement was carried out. In Figure 1, IR absorption spectra before and after grafting are shown. The adsorption at 1657, 1555 and $1311 cm^{-1}$ in the spectrum of chitin are due to the amide groups in chitin, which can be assigned as the amide I, II, and III bands, respectively. The absorption of CH_2 wagging is also contained in the band at $1311 cm^{-1}$. Examination the IR spectrum carefully, it can be found that the amide I band is further separated to two absorptions at 1657 and $1625 cm^{-1}$ [7]. As can be seen in Fig. 1, after grafting, the absorption band of nitrile group due to polyacrylonitrile grafted chains on chitin is observed at $2247 cm^{-1}$. This absorption band is taken as evidence of grafting of AN onto the chitin backbone. The relative absorption intensities of the absorptions at 1657 and $1625 cm^{-1}$ are influenced by PAN branches.

Thermal analysis

Thermal properties of the chitin and its graft copolymer were obtained by TGA (Figure 2) and DSC (Figure 3). In general, the TGA and DSC curves for the ChAN show characteristic patterns distinctly different from the ungrafted chitin. ChAN has much more thermal stability than original chitin up to 700°C (as evident from a lower wt% loss - 1.34% residue in the case of chitin, 29.77% residue in the case of ChAN at 700°C). Initial decomposition takes place at 382°C and 304°C for chitin and ChAN, respectively. It is clear that grafting of AN onto chitin not only increases significantly the thermal stability of chitin, but also changes remarkably the characteristic TGA and DSC patterns of chitin.
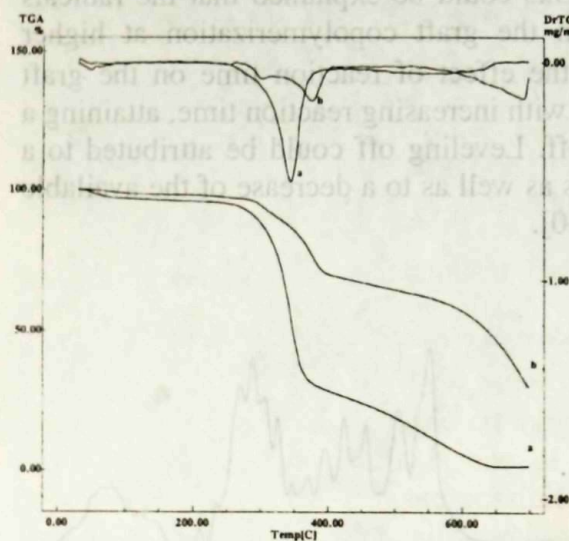

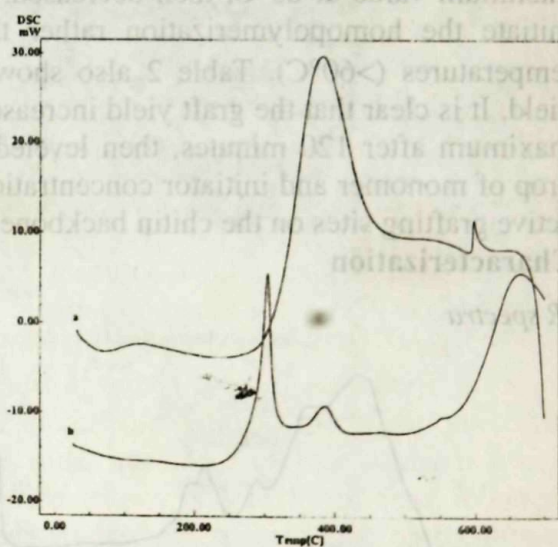Figure 2. TGA and DTG (derivative themogravimetric) curves of (a) chitin and (b) ChAN

Figure 3: DSC curves of (a) chitin, (b) ChAN.

CONCLUSION

Acrylonitrile was successfully grafted onto chitin in a suspension system by chitin thiocarbonate-Fe(II)-H_2O_2 system as a redox initiator. The optimal conditions for an effective grafting reaction have been worked out as follows: [Fe^{2+}], 0.15 g/100 ml; [H_2O_2], 0.3%; pH, 3; time, 120 min; temperature, 70°C. The structural changes of

the chitin after grafting were confirmed by IR spectroscopy and thermal analysis (TGA and DSC).

REFERENCES

[1]. M. Sugimoto, M. Morimoto, H. Sashiwa, H. Saimoto, Y. Shigemasa. *Carbohydrate Polymers*, **36**, p.49-59 (1998).

[2]. K. Kurita, S. Inoue, K. Yamamura, H. Yoshino, S. Ishii and S. Nishimura and K. Shimoda. *Macromolecules*, **25**, p.3791-3794 (1992).

[3]. Y. Shigeno et al., *J. Macromol. Sci. Chem.*, A17, p. 571 (1982).

[4]. A. Takahashi, Y. Sugahara, Y. Hirano, *J. Polym. Sci. Part A: Polym. Chem.* **27**, p. 3817 (1989).

[5]. K. Kurita, M. Kawata, Y. Koyama, S. Nishimura. *J. Appl. Polym. Sci.*, **42**, p. 2885 (1991).

[6]. A. Lagos, M. Yazdami-Pedram, J. Reyes. *J. Macromol. Sci., Pure Appl. Chem.*, A29, p.1007 (1992).

[7]. Longdi Ren, Y. Miura, N. Nishi & S. Tokura. *Carbohydrate Polymers*. **21**, p. 23-27 (1993).

[8]. Longdi Ren & Seiichi Tokura. *Carbohydrate Polymers*. **23**, p.19-25 (1994).

[9]. Lớgia Furlan, Valfredo T. de Fòvere and Maro C. M. Laranjeira. *Polymer*, Vol. 37, N°5, p. 843-846 (1996).

[10]. ALy Sayed Aly, Byong Dae Jeon, Yun Heum Park. *J. Appl. Polym. Sci.*, **65**, p.1939-1946 (1997).

[11]. R. H. Hackman. *Austr. J. Biol. Sci.*, **7**, p.168 (1958).

[12]. Yasumasa Morita, Yasusato Sugahara, Masaru Ibonai, Akira Takahashi. *J. Appl. Polym. Sci.*, **71**, p.189-195 (1998).

[13]. Frộdộric Niola, Nuria Basora, Esteban Chornet and Pierre Franõois Vidal. *Carbohydrate Research*, **238**, p.1-9 (1993).

ĐIỀU CHẾ VÀ ĐÁNH GIÁ COPOLYME GHÉP TRÊN CƠ SỞ α-CHITIN VÀ ACRYLONITRIL CHO XỬ LÝ NƯỚC THẢI

1. Phản ứng đồng trùng hợp ghép acrylonitril với α-chitin

Đã điều chế thành công một loại vật liệu ghép trên cơ sở chitin (chitin tách từ vỏ tôm) và acrylonitril trong dung dịch nước ở dạng huyền phù sử dụng hệ khơi mào chiitin thiocarbonate-Fe(II)-H₂O₂. Các điều kiện tối ưu cho phản ứng copolyme ghép acrylonitril lên chitin đã được nghiên cứu bằng cách khảo sát các ảnh hưởng của nồng độ muối Mohr, nồng độ hydro peoxit và nồng độ monome cũng như ảnh hưởng của pH dung dịch, thời gian và nhiệt độ phản ứng đến tỷ lệ khối lượng mạch ghép so với chitin. Khảo sát sự thay đổi cấu trúc của chitin sau phản ứng copolyme ghép bằng phổ hồng ngoại và phân tích nhiệt (TGA và DSC).