Grafting of Cellulose Extracted from Kenaf Using *Xanthate Method*

Sherif M.A.S. Keshk[a,b,*]

[a]*King Khalid University, Faculty of Science, Chemistry Department, P.O. Box 9004, Abha 61413, Saudi Arabia*

[b]*Ain-Shams University, Institute of Environmental Studies and Research, Basic Science Department, Abbassia, Cairo 11566, Egypt*

Abstract: Mass spectra of reconstructed ion chromatogram (MRIC) technique are used to follow up the grafting copolymerization of 1-vinyl-2-pyrrolidinone (VP), 1-vinyl-3-anisylidine-2-pyrrolidinone (VAP) and ethylmethacrylate (EMA) and cellulose extracted from kenaf using xanthate method. Grafting is carried out under ionic and/or free radical mechanism conditions. Factors affecting grafting yield such as temperature, sodium hydroxide concentration, liquor ratio, carbon disulfide concentration, monomer and grafting time have been studied.

Keywords: Cellulose, Cellulose xanthate, Ethylmethacrylate, 1-vinyl-2-pyrrolidinone, 1-vinyl-3-anisylidine-2-pyrrolidinone.

INTRODUCTION

Kenaf (*Hibiscus cannabinus* L.) is an annual herbaceous crop of the Malvaceae family, of which cotton and okra are also members. The traditional uses of kenaf focus on its production for fibre used in making rope, sacks, canvas and carpets [1-3]. New applications for kenaf have been developed in the pulp and paper industry, for oil absorption, as a potting medium, in the manufacture of broadcloth, in filtration, and as an additive in animal feed [4]. Chemical modification of cellulose by graft copolymerization has generated interest among researchers because few commoner molecules change significantly a number of characteristics of the original natural polymer [5-8]. Thus new areas of the application might be opened for the modified cellulose-type material. Being a polymer itself, cellulose can be copolymerized only with block or grafting procedure. The block copolymerization of cellulose essentially modifies its physical structure and therefore cannot be used. A graft copolymer is a system comprised of a backbone material to which a second polymer is attached at intervals along the chain. Most of graft copolymerization examined so far, describe the use of cotton or regenerated cellulose or wood pulp as the substrate [9-11]. There are a few papers about the grafting of Kenaf bast fiber [12-14]. Polyacrylonitrile was grafted onto kenaf fibers in aqueous media by ceric ion-*p*-xylene redox system. The graft yield dependence on *p*-xylene concentration in the range 1.8-45.0 × $10^{-4}M$ showed a minimum accompanied by an enhanced yield [15]. Moreover, Graft copolymers of acrylonitrile on kenaf fibers were obtained in an aqueous medium by the use of allyl alcohol and allyl chloride in combination with ceric ion as redox pairs. Radical polymerization has several disadvantages [15]. Reproducibility of this method is poor and there is little control over the grafting process. The net result is that grafting involves only a few high molecular weight molecules with a low level of grafting substitution. The graft copolymerization reactions showed distinct features that were associated with different initiating species derived from the redox pairs. It is important to choose synthetic polymer those containing functional groups that can potentially interact with the hydroxyl groups of cellulosic chain, such as polyamides, polyesters and vinyl polymers. In this paper, grafting of synthetic vinyl polymers onto cellulose extracted from kenaf fiber offers the potential of preparing a new class of engineering materials. Properties of the derived graft polymers may be tailored to meet certain specifications by controlling parameters such as the molecular weight of the grafted side chains, the number of grafting side chains and the type of grafted side chain.

MATERIAL AND METHODS

Source Material

A frost-killed kenaf (*Hibiscus Cannabinus*) variety, Tainung-2 was grown in Nankoku, Kochi, Japan (latitude 33°N) and was harvested in November 2000 (180 days after planting) the plant were frozen immediately after harvesting and then freeze-dried. The stems were separated manually into bast and core. The bast fibres were cut into 30 mm lengths prior to treatment.

---

*Address correspondence to this author at the King Khalid University, Faculty of Science, Chemistry Department, P.O. Box 9004, Abha 61413, Saudi Arabia; Tel: +966-559754436; Fax: +966172417056;
E-mail: keshksherif@gmail.com

ISSN: 1814-8085 / E-ISSN: 1927-5129/14

Pulping Methods

Various chemical combinations and conditions were employed for processing kenaf bast fibre [14]. Treatment that used a sequence of ammonium oxalate, sodium hydroxide and acidic sodium chlorite are applied.

Synthesis and Graft Copolymerization

i. Synthesis 1-vinyl-3-anisidine 2-pyrrolidinones (VAP) and 1-vinyl-Benzidine2-pyrrolidinones (VBP)

10% Sodium hydroxide (15 ml) was added dropwise within 15 min to a stirring mixture of 1-vinyl-2-pyrrolidinone (1.11g) and anisaldehyde or benzaldehyde (0.01 mole) in ethanol (30 ml). The reaction mixture was further stirred for 4 hr and left overnight at room temperature. The mixture was poured into ice water then the precipitate was filtered off and recrystallized from ethanol.

Polymer VAP (Yield 80%) m.p.142-144 °C. Elemental analysis of VAP:

Found: C; 73.41; H, 6.60; N, 6.30.

Calculated: C; 73.36; H, 6.55; N, 6.11.

IR (KBr): 1660 cm^{-1} (μ CO), 1580-1610 cm^{-1} (μ C=C).

H^1NMR (DMSO): 3.1-3.6 ppm (txt. 4H heterocyclic moiety), 3.80 ppm (s, 3H, $-OCH_3$) and 6.88-7.66 ppm (m, 8H, olefinic and Ar-H).

Mass spectrum: m/z 229 (100%) molecular ion peak, 200 (6%), 146 (98%), 115(20%) and 76 (15%) that characterized to the positive ion or positive ion free radical of Polymer VBP (Yield 83%) m.p.128-130 °C. Elemental Analysis of VBP:

Found: C; 78.40; H, 6.60; N, 7.30.

Calculated: C; 78.39; H, 6.53; N, 7.03.

ii. Graft Copolymerization of Vinyl Monomers onto Cellulose with the Use of Ionic Xanthate Method

Cellulose (0.25 gm) was placed in well stopper round bottom flasks (50 ml), and then 0.75 ml of purified carbon disulfide was added followed by 1.5 ml NaOH (17.5%) with light hand shaking every 15 min for 1 hr at 30°C. Then 0.75 ml vinyl monomer was added with light hand shaking every 15 min for 2hr. The grafted cellulose was precipitated by 5ml distilled acidified water, then the mixture was filtered and washed well by distilled water and dried at 60°C. The percentage of grafting yields were calculated according to the following equation

$$\text{Grafting yield\%} = (G-P)/DX\ 100$$

Where (G) is the weight of the product after copolymerization in gm, (D) is the weight of dry cellulose in gm.

iii. Grafting Copolymerization of Vinyl Monomers onto Cellulose with the Use of Xanthogenate/H_2O_2 Redox System

The free radical xanthate method of grafting was carried out as follows: 0.25 gm cellulose was placed in 50 ml stopper round bottom flask. 0.75 ml of purified CS_2 was added followed by 1.5 ml NaOH (17.5%) after 2 min, the flask was lightly covered and occasionally light hand-shaking every 15 min during the time of formed cellulose xanthate, (1hr.at 30°C) (30 %) (vol/vol) was added followed by 0.75 ml vinyl monomer. The grafting cellulose was precipitated by 5 ml distilled acidified water and washed well by distilled water and dried at 60°C.

IR Spectroscopy

The cellulose extracted from kenaf prepared according to Keshk *et al.* [15]. FT-IR spectra were obtained with a Nihon FT-IR-480 spectrometer. The reproducibility of the spectra was verified on a three-sample preparation; from 64 to 100 scans were taken with a resolution of 0.5 cm^{-1}.

Mass Spectra

Mass spectra of samples were recorded on Finnegan SSQ 7000 spectrometer.

RESULT AND DISCUSSION

Effect of Monomer

The percent of grafted yield in both ionic and free radical increased with the increase of monomer concentration, whereas with more than 60% the graft yield percent decreased. Furthermore, the percentage of graft efficiency decreases with the increase of monomer concentration, due to graft efficiency depend on the monomer concentration as reported by Kaur *et al.* (1998) that explained in terms of the monomer solubility and polymerizability.

Effect of Initiator

The percent of graft yield and graft efficiency increase with the increase of hydrogen peroxide concentration up to 5% whereas, beyond this range, the graft yield and graft efficiency decreased. This is may be explained by its participation in the termination of grafting onto cellulose [10].

Effect of Temperature

The percent of graft yield and graft efficiency increased with the increase of the temperature from 40° for ionic grafting of VAP and 60° for free radical grafting of VAP, to 50° for ionic grafting of EMA and 60° for free radical grafting. While in case of VP the temperature is the best at 35° and 50° for both ionic and free radical grafting, respectively. The increase in graft yield and efficiency percent at high temperature in free radical grafting, may be a result of the increase in the rate of production of active free radical. Which increase the number of grafting sites at a higher rate, so the rate of diffusion of monomer into the cellulose backbone increases. However, this behavior can be explained as increase thermal decomposition rate of initiator increased with the initiator efficiency the resulting polymer macro radicals' concentration increase. Whereas, the grafting yield decrease with increase the temperature beyond 60° for VAP, VP and 50° for EMA is due to the molecular motion of peroxide increased with increased temperature, resulting in increased radical decay.

Effect of Catalyst

The effect of catalyst that is, NaOH concentration on the graft yield and efficiency percent is studied. The percent graft yield and graft efficiency increased with the increase of NaOH concentration up to 4% and then it decreased gradually as NaOH concentration increased. The plausible explanation of such behavior is that NaOH in the grafting medium assisted the grafting both by causing inter- and intra-crystalline swelling of the substrate and by acting as catalyst in the swelling of cellulose leading to uncoiling of the chains and improvement of the monomer accessibility. A higher concentration of alkali may cause degradation of the backbone chain of cellulose as well as of the graft chains, so the graft yield percent was decreased.

Effect of Time

The percent of graft yield and graft efficiency increased with the increase of the time up to 300 min and beyond which it decreased. This tendency of graft to first increase, attain a maximum value and then decrease may be accounted for by the increasing extents of initiation and propagation of the reaction initially with time (Merlin, 2003).

Mass Spectroscopy

Grafting polymerization of cellulose xanthate of kenaf cellulose was flow up usually by the change of υCO andυOH of the end products. In this study, we flow up the grafting copolymerization of vinyl monomers onto cellulosic xanthate using Mass spectra of reconstructed ion chromatograph (MRIC). MRIC of each cellulosic materials characterized by area at different retention time and each area has a fixed base peak (100%) in mass spectra that is characterized to monomer, cellulose and cellulose xanthate. Reconstructed ion chromatogram (RIC) for cellulose (Figure **1**) exhibited two peaks at retention times 1.35 and 2.25, these suggested to be the amorphous and crystalline phases respectively. The percentage of the amorphous to the crystalline phases is 15.35 % approximately. It was found that fragmentation of amorphous and crystalline phases are relatively the same, where the base peak at m/e 55 is characterized to positive ion or positive ion free radical CH_2=CHCO. In cellulose xanthate three peaks are appeared. The main peak appears at retention time 1.58 and other two peaks at retention times 1.32 and 2.15 with ratio 10:5% relative to the main peak. All the fragmentations of cellulose are present and the base peak of fragmentation appears at m/e 76 due to positive ion or free radical positive ion of CS_2. Polymerization of bacterial cellulose xanthate with N-vinyl-pyrrolidine (VP) showed two peaks for each grafting product. The main peaks at retention time 1: 17- 1: 38 while the minor peaks at retention time 2.08. The fragmentation of the main peaks include the fragmentations of cellulose xanthate and monomer (VP) and the base peak at m/e 112 where the molecular ion peak of monomer added hydrogen atom. Fragmentation of the minor peaks did not appeared fragmentation pattern of N-vinyl pyrrolidinone. RIC of cellulose xanthate/poly ethyl methacrylate showed main peak at retention time 2.04 and two minor peaks at retention times 1.28 and 1.44.the fragmentation of the main peak exhibits two base peaks at m/e 55 and 72 characterized to fragments CH_2=CH-CO and $C_3H_4O_2$ due to the fragmentation of cellulose and ethyl methacrylate. On the other hand, the mass spectra of the minor products exhibited a base peak m/e 76 characterized to xanthate. Copolymerization of cellulose with EMA and VP gave products separated by RIC at retention time 1.11, 1.39 and 1.56 in ratio 0.12: 1: 0.08. Mass fragmentation of the peak at retention time 1.11 shows

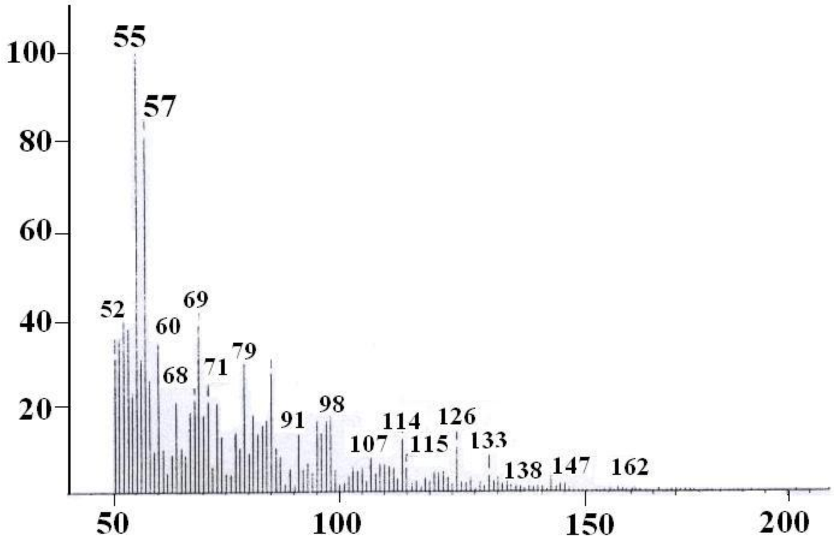

Figure 1: Mass Spectrum of Cellulose Extracted from Kenaf.

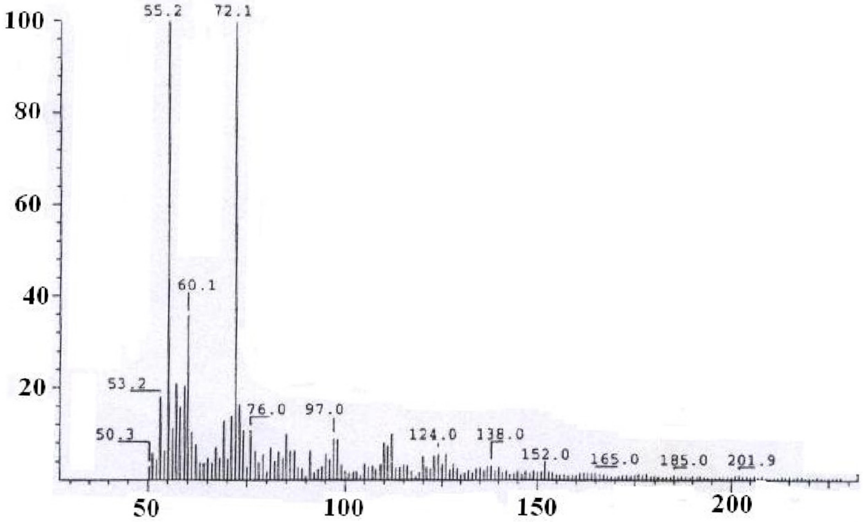

Figure 2: Mass spectrum of Cellulose Xanthate.

Table 1: Optimum Conditions of Grafting Yield on Cellulose from Kenaf

Factors	VP		VAP		EMA	
	Ionic	Free radical	Ionic	Free radical	Ionic	Free radical
Temperature,°C	25	25	30	40	50	40
NaOH/100ml	22	24	22	20	175	20
Liquor ratio	1:6	1:6	1:8	1:6	1:6	1:6
Amount of cell.: CS_2	13	1:3	1:4	1:4	1:4	1:3
Grafting time (min.)	240	240	240	240	240	240
Monomer Conc. (w/w)Cell/Monomer	1:6	1:6	1:6	1:6	1:6	1:6
Dluent Monomers/ Dioxan v/v	3:3	3:1	Not recorded	Not recorded	3:1	3:0
Effect of H_2O_2 Conc.	-	5	Not recorded	Not recorded	-	5

the fragmentation pattern of vinyl pyrrolidine. Also, mass fragmentation of the peak at retention time 1.39 shows the fragmentation pattern of VP. The mass fragmentation of peak at retention time 1.56 shows the fragments at 111 and 72 characterize to VP and EMA in ratio 1: 0.76. On grafting 1-vinyl-3-anisylidine-2-pyrrolidinone (VAP) on cellulose xanthate, three peaks are appeared at retention times 1.33, 1.53 and 1.82 in the ratio 1:0.11: 0.03. These corresponding to mass fragmentation of VAP and cellulose xanthate, respectively.

ACKNOWLDGEMENT

Author would like to thank King Khalid University and King Abdul Aziz City for Science and Technology for their miscellaneous help during this study. This project (AT-34-95) was jointly supported by King Abdul Aziz City for Science and Technology (KACST).

REFERENCES

[1] Chapiro A. Chemistry of polymeric system. John Wiley and Sons, New York 1962.

[2] Nasef M, Saidi H, Nor H, Foo M. Cation Exchange Membrane by Graft Copolymerization of styrene onto PFA copolymer Film. J Appl Polym Sci 2000; 76: 1-11. http://dx.doi.org/10.1002/(SICI)1097-4628(20000404)76:1<1::AID-APP1>3.0.CO;2-4

[3] Gupta B, Anjum N, Sen K. Development of membrane by Grafting of Acrilamide into Polyethylene films. J Appl Polym Sci 85: 282-291. http://dx.doi.org/10.1002/app.10573

[4] Mulder M. Basic Principles of membrane Technology. Kluwer Academic Publishers 1996. http://dx.doi.org/10.1007/978-94-009-1766-8

[5] Silverstein R, Basler G, Morrii C. Spectrometric identification of polymer. John Wiely and Sons 2000.

[6] Choi Y, Yeonghee A, Sung K, Hong J, Kim I, Moon S. Preparation and characterization of acrylic acid-treated bacterial cellulose cation-exchange membrane. J Chem Technol Biotech 2003; 79: 79-84. http://dx.doi.org/10.1002/jctb.942

[7] Eromosele C, Agbo A. Grafting acrylonitrile on kenaf fibers using ceric ion-p-xylene redox pair. J Appl Polym Sci 1999; 73: 1751-55. http://dx.doi.org/10.1002/(SICI)1097-4628(19990829)73:9<1751::AID-APP16>3.0.CO;2-9

[8] Elisabet H, Lindström T. Capillary electrophoresis analysis of poly(ethylene glycol) and ligand-modified polylysine gene delivery vectors. Anal Biochem 2007; 363: 204-209. http://dx.doi.org/10.1016/j.ab.2007.01.024

[9] Elisabetta P, Vicini S, Pedemonte E, Gentile E, Cocca M, Martusc E. The synthesis of CDA-g-PMMA copolymers through atom transfer radical polymerization. Polymer 2004; 45: 7091-97. http://dx.doi.org/10.1016/j.polymer.2004.08.042

[10] Guo Y, Sun Y, Gu J, Xu Y. Photoinduced graft copolymerization of polymer surfactants based on hydroxyethyl cellulose. J Photochem Photobiol A 2007; 12: 211-15.

[11] Hongliang K, Wenyong L, Benqiao H, Dawa S, Lin M, Huang Y. New method for the covalnt immobilization of a xylanase by radical grafting of acrylamide on cellulose acetate membranes. Enzyme Microbial Technol 2006; 39: 125-130. http://dx.doi.org/10.1016/j.enzmictec.2005.10.007

[12] Zhengxing L, Wang L, Huang Y. Synthesis of amphiphilic ethyl cellulose grafting poly(acrylic acid) copolymers and their self-assembly morphologies in water. Polymer 2006; 47: 7927-34. http://dx.doi.org/10.1016/j.polymer.2006.09.017

[13] Sarbu A, Norberta de Pinho M, Maria do Rosário F, Goncalves F, Udrea I. Synthesis and mechanical characterisation of cellulose based textiles grafted with acrylic monomers. Eur Polymer J 2006; 42: 312-16.

[14] Keshk SMAS, Suwinarti W, Sameshima K. Physical Structure Characterization of High Viscosity Kenaf Bast Pulps. Japan Tappi J 2005; 59: 75-79. http://dx.doi.org/10.2524/jtappij.59.1833

[15] Keshk SMAS, Suwinarti W, Sameshima K. Physicochemical Characterization of Different Treatment Sequences on Kenaf Bast Fiber. Carbohydrate Polymer 2006; 65: 202-207. http://dx.doi.org/10.1016/j.carbpol.2006.01.005

Received on 10-03-2014 Accepted on 02-07-2014 Published on 23-07-2014

http://dx.doi.org/10.6000/1927-5129.2014.10.44