Carbohydrate Polymers 90 (2012) 930–936

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Preparation and characterization of poly(acrylic acid)-hydroxyethyl cellulose graft copolymer

E.S. Abdel-Halim [a,b,*]

[a] Petrochemical Research Chair, Chemistry Department, College of Science, King Saud University, Riyadh 11451, P.O. Box 2455, Saudi Arabia
[b] Textile Research Division, National Research Center, Dokki, Cairo, Egypt

ARTICLE INFO

Article history:
Received 1 May 2012
Received in revised form 20 May 2012
Accepted 10 June 2012
Available online 19 June 2012

Keywords:
Cellulose
Acrylic acid
Grafting
Potassium bromate
Thiourea dioxide

ABSTRACT

Poly(acrylic acid) hydroxyethyl cellulose [poly(AA)-HEC] graft copolymer was prepared by polymerizing acrylic acid (AA) with hydroxyethyl cellulose (HEC) using potassium bromate/thiourea dioxide ($KBrO_3$/TUD) as redox initiation system. The polymerization reaction was carried out under a variety of conditions including concentrations of AA, $KBrO_3$ and TUD, material to liquor ratio and polymerization temperature. The polymerization reaction was monitored by withdrawing samples from the reaction medium and measuring the total conversion. The rheological properties of the poly(AA)-HEC graft copolymer were investigated. The total conversion and rheological properties of the graft copolymer depended on the ratio of $KBrO_3$ to TUD and on acrylic acid concentration as well as temperature and material to liquor ratio. Optimum conditions of the graft copolymer preparation were 30 mmol $KBrO_3$ and 30 mmol TUD/100 g HEC, 100% AA (based on weight of HEC), duration 2 h at temperature 50 °C using a material to liquor ratio of 1:10.

1. Introduction

Synthesis of polyvinyl-polysaccharides composites has been investigated by a number of authors (Abdel-Halim, Abdel-Mohdy, et al., 2011; Abdel-Halim, El-Rafie, & Al-Deyab, 2011; Abdel-Halim, Emam, & El-Rafie, 2008; Chen et al., 2005; Hashem, Sokkar, Abdel-Halim, & Gamal, 2005; Joshi & Sinha, 2007). These composites have been synthesized to expand the market of polysaccharides-based products. These products are employed as reclaimable sizing agents (Hebeish, Higazy, El-Shafei, & Sharaf, 2010a; Mohamed, Amr, Knittel, & Schollmeyer, 2010) and substituent for the alginate thickener in the reactive printing (Gong et al., 2011; Turk & Schneider, 2000). Grafting of synthetic polymers onto biopolymers results in novel products having wide range of applications. This way of chemical modification yields new molecules with desirable properties of both biopolymer and synthetic polymer. Modern technologies require materials with precisely tuned properties by varying a set of parameters during synthesis, i.e. tailor-made materials (Abdel-Halim & Al-Deyab, 2011b; Abdel-Halim, Fahmy, & Fouda, 2008; El-Tahlawy, Abdel-Halim, Hudson, & Hebeish, 2007; Hebeish, El-Rafie, Abdel-Mohdy, Abdel-Halim, & Emam, 2010; Ibrahim, Abdel Moneim, Abdel Halim, & Hosni, 2008; Sokkar, Abdel-Halim, Aly, & Hashem, 2004). Grafted polymers fit well in this category of materials as their properties can be precisely controlled by controlling the percentage grafting. Chemical grafting is one of the most effective methods of modifying structure and properties of biopolymers. Graft copolymerization of natural polysaccharides is becoming an important resource for developing advanced materials as it can improve the functional properties of natural polysaccharides (Ly, Bras, Sadocco, Belgacem, Dufresne, & Thielemans, 2010; Meshram, Patil, Mhaske, & Thorat, 2009; Rui-He, Wang, Wang, Yang, Zeng, & Ding, 2006; Szamel, Domjan, Klebert, & Pukanszky, 2008; Zhu, Dong, Wang, & Wang, 2010). The grafted polymers are usually synthesized by conventional redox grafting methods (da Silva, de Paula, & Feitosa, 2007; Hebeish, Abd El-Thalouth, El-Kashouti, & Abdel-Fattah, 2003; Kaith, Singha, & Kalia, 2007; Kang, Cai, & Liu, 2006; Singh, Tiwari, & Sanghi, 2005), by microwave irradiation (Masuhiro, Shafiul, Takayuki, Alessandra, & Giuliano, 2005; Singh, Tiwari, Pandey, & Singh, 2007), by γ-ray irradiation (Geresh, Gdalevsky, Gilboa, Voorspoels, Remon, & Kost, 2004; Wang, Chen, Zhang, & Yu, 2008) or by using electron beam (Vahdat, Bahrami, Ansari, & Ziaie, 2007).

Cellulose is the main constituent of cell wall in lignocellulosic plant, in which the cellulose content is 23–53% on a dry weight basis, less than that in cotton, which is almost made of pure fibrous cellulose (Knauf & Moniruzzaman, 2004). In the

* Correspondence address: National Research Center, Dokki, Cairo, Egypt. Tel.: +20 108113477.
E-mail address: essamya@yahoo.com

0144-8617/$ – see front matter © 2012 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.carbpol.2012.06.022

lignocellulosic materials, cellulose is embedded in a gel matrix composed of hemicelluloses, lignins, and other carbohydrate polymers (Hanley, Revol, Godbout, & Gray, 1997; Yu, Liu, Shen, Jiang, & Huang, 2005). The isolation of highly pure cellulose has been the subject of extensive studies for many years because of the complexity of cell wall structure (Brendel, Iannetta, & Stewart, 2000; Sun & Hughes, 1998). The use of cellulose obtained from sugarcane bagasse for production of cellulose derivatives has been reported in the literature (Gurgel, de Freitas, & Gil, 2008; Shaikh, Pandare, Nair, & Varma, 2009; Wang, Li, Xiao, & Wu, 2009). Also our research group has been working on demonstrating the viability of chemical recycling of cellulosic agricultural waste and industrial wastes for the production of higher value products (Abdel-Halim, 2012a, 2012b; Abdel-Halim, Abdel-Mohdy, Al-Deyab, & El-Newehy, 2010; Abdel-Halim & Al-Deyab, 2011a, 2011c, 2011d, 2012; Abdel-Halim, El-Rafie, & Kohler, 2008; Abdel-Halim, Fouda, Hamdy, Abdelmohdy, & El-sawy, 2010; Abdel-Halim, Konczewicz, Zimniewska, Al-Deyab, & El-Newehy, 2010a; Abdel-Mohdy, Abdel-Halim, Abu-Ayana, & El-Sawy, 2009; Fahmy & Abdel-Halim, 2010; Hashem, Abdel-Halim, El-Tahlawy, & Hebeish, 2005; Hashem, Abdel-Halim, & Sokker, 2007; Hebeish, Ramadan, Abdel-Halim, & Abo-Okeil, 2011). Few commercial uses for the excess bagasse have been developed and its accumulation presents a waste problem for the sugar industry. The same is the case with wheat and rice straw, cereal straws, cotton stalks, etc. One area where tremendous amount of research has been devoted pertains to the fractionation of agricultural biomass into its constituents, i.e. cellulose, hemicellulose, and lignin in what is best described as a bio-refinery. Each of these fractions can then be separately value-added by making industrially important derivatives. For example, cellulose can be converted into cellulose esters (Shaikh et al., 2009), which have wide ranging applications as biodegradable plastics, textile fibers, films, etc. and cellulose ethers (Vieira et al., 2009) which find many industrial applications as thickeners.

Hydroxyethyl cellulose (HEC) is a nonionic, water-soluble polymer that can thicken, suspend, bind, emulsify, form films, stabilize, disperse, retain water, and provide protective colloid action. It is readily soluble in hot or cold water and can be used to prepare solutions with a wide range of viscosities. Hydroxyethyl cellulose has many industrial applications like contributing a desired body in paints (Dal-Bó, Laus, Felippe, Zanette, & Minatti, 2011), textile finishing (Gorgieva & Kokol, 2011), thickening cement mortar (Patural, Marchal, Govin, Grosseau, Ruot, & Devès, 2011) and paper making (Kugge, Craig, & Daicic, 2004). In the manufacture of hydroxyethyl cellulose, purified cellulose is reacted with sodium hydroxide to produce swollen alkali cellulose. This alkali-treated cellulose is more chemically reactive than cellulose. By reacting the alkali cellulose with ethylene oxide, a series of hydroxyethyl cellulose ethers is produced. In this reaction, the hydrogen atoms in the hydroxyl groups of cellulose are replaced by hydroxyethyl groups, which confer water solubility to the product when the molar substitution reaches certain value.

Recently we have studied the conversion of sugarcane bagasse cellulose to valuable products, hydroxyethyl cellulose (HEC). To fulfill more industrial application to the HEC obtained from the purified sugarcane bagasse, we use it in the current study as a starting material for preparation of poly(AA)-HEC composite. The composite is a term given to the reaction product of the HEC, the acrylic acid (AA) and the initiator when all these ingredients are present in aqueous system for polymerization. Based on that, the present study is concerned with polymerization of acrylic acid with hydroxyethyl cellulose using $KBrO_3$-TUD redox system. The polymerization reaction will be carried out under different conditions including concentration of AA, $KBrO_3$, TUD, material to liquor ratio and temperature of polymerization.

2. Experimental

2.1. Materials

2.1.1. Cellulosic raw material

Fresh bagasse was washed thoroughly in running water to make sure that all sugar residues were washed off to minimize microbial attack. The washed bagasse was dried in sunny area until it is completely dry and then ground into fine particles using Fritsch mill, Type 15.302 (Germany). The ground bagasse was subjected to alkali treatment followed by bleaching with sodium chlorite activated with hexamethylenetetramine (Abdel-Halim, 2012b). The so bleached ground bagasse was used as a starting material for the preparation of hydroxyethyl cellulose, according to a reported method (Zahran, Abdel-Halim, & El-Rafie, 1998).

2.1.2. Chemicals

Acrylic acid (AA) potassium bromate, thiourea dioxide (TUD), sulphuric acid, sodium thiosulphate, potassium iodide, and potassium bromide were laboratory grade reagents.

2.2. Preparation of poly(AA)-HEC composite

Hydroxyethyl cellulose dissolved in water was stirred well and the temperature was raised to the desired polymerization temperature. When the desired reaction temperature was attained, known concentrations of acrylic acid and aqueous solution of the initiation components (potassium bromate/thiourea dioxide) were added to the hydroxyethyl cellulose solution. A material to liquor ratio of 1:10 was employed and the reaction was allowed to proceed under continuous stirring for 120 min.

2.3. Testing and analysis

2.3.1. Total conversion

The percentage total conversion was calculated by quantitative estimation of the acrylic acid double bonds, according to a reported method (Sailaja & Murthy, 2010).

2.3.2. Apparent viscosity

The apparent viscosity of the poly(AA)-HEC composite was evaluated using Bohlin Rotational Viscometer at different rates of shear.

3. Results and discussion

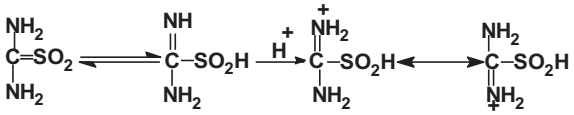
3.1. Preparation of poly(AA)-HEC graft copolymer

The synthesis of poly(AA)-HEC graft copolymer was achieved using a very efficient potassium bromate-thiourea dioxide redox initiation system. Effect of the concentrations of $KBrO_3$, TUD and AA, the material to liquor ratio, the polymerization temperature and polymerization duration were studied. However, before going into detailed investigation of these parameters, it seems logical to shed some insight on the mechanisms involved in the polymerization reaction using the aforementioned initiation system.

3.2. Tentative mechanism

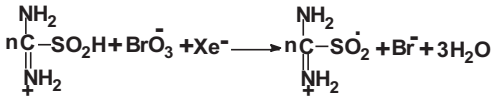
When potassium bromate (oxidant) is coupled with thiourea dioxide (reductant), in acidic medium, a very efficient redox system is established. In the presence of AA as a monomer and hydroxyethyl cellulose which contains functional hydroxyl groups in the cellulose structure and the terminal hydroxyethyl group, the primary free radical species brought about by decomposition of the redox system can initiate homopolymerization of AA as well as

grafting of the latter onto the HEC molecules. Specifically the polymerization process involves conversion of thiourea dioxide, in acidic medium, to isothiourea dioxide (Eq. (1)).



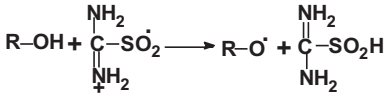
(1)

Isothiourea dioxide reacts with bromate anion to generate isothiourea dioxide free radicals (Eq. (2)).



(2)

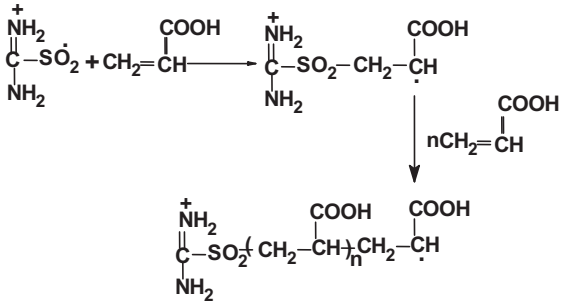
The isothiourea dioxide radicals attack functional hydroxyl groups of HEC to form HEC free radicals (Eq. (3)).



(3)

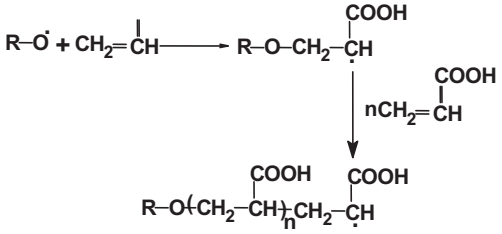
where R-OH = Cell—OH or Cell—O—CH_2CH_2—OH.

Furthermore, isothiourea dioxide can strongly initiate homopolymerization of AA molecules (Eq. (4)).



(4)

The reaction of hydroxyethyl cellulose free radical with AA initiates the grafting reaction along the HEC backbone (Eq. (5)).

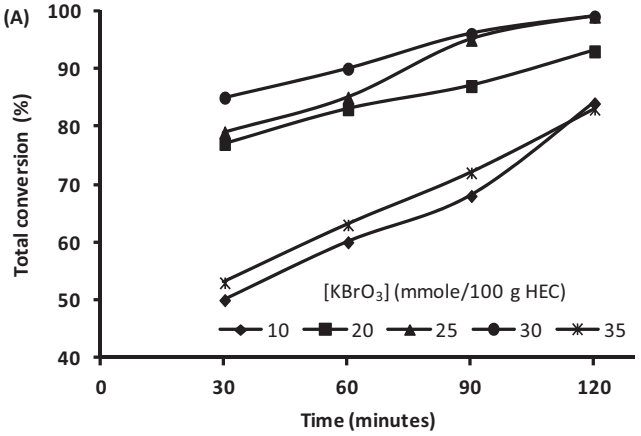


(5)

It should be mentioned that $KBrO_3$ plays an important role other than initiation of AA polymerization, namely oxidation of HEC molecules, particularly at higher bromate concentration. Furthermore, the Br_2 molecules liberated at higher bromate concentration may also attack and oxidize the HEC with subsequent degradation of HEC molecules (Eq. (6)).

$$BrO_3^- + 5Br + 6H^+ \rightarrow 3Br_2 + 3H_2O \quad (6)$$

Taking the above tentative mechanisms into consideration, the factors affecting the preparation of the poly(AA)-HEC composite were studied. The results obtained are given below along with their appropriate discussion.



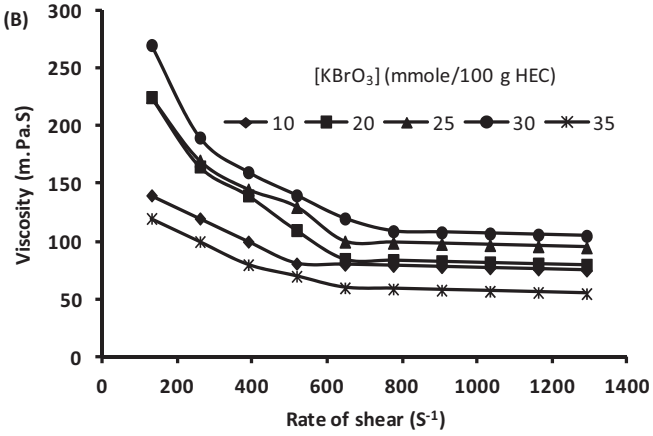


Fig. 1. Effects of $KBrO_3$ concentration on: (A) total conversion and (B) viscosity.

3.3. Effect of initiator components concentrations

3.3.1. Potassium bromate concentration

Fig. 1A shows the dependence of the extent and rate of polymerization of acrylic acid, expressed as percent total conversion, on $KBrO_3$ (oxidant) concentration. It is observed (Fig. 1) that, regardless of the used $KBrO_3$ concentration, the total conversion is characterized by an initial fast rate followed by a slower rate. It is obvious that the total conversion increases with the increase in $KBrO_3$ concentration up to 30 mmol/100 g HEC and decreases significantly with further increase in $KBrO_3$ concentration. Enhancement of acrylic acid conversion to poly(acrylic acid) could be interpreted in terms of the redox process under question. The data indicate that maximum total conversion is attained at equimolar ratio of $KBrO_3$ and TUD 30:30 mmol/100 g HEC. The enhancement in the polymerization reaction at this critical concentration could be explained in terms of creation of larger amounts of free radicals (Eqs. (2)–(4)). Inhibition of the polymerization reactions by liberated Br_2 (Eq. (6)) as well as participation of the bromate ion at higher concentrations in the termination process may explain the lowering of the total conversion of AA when $KBrO_3$ concentration higher than 30 mmol/100 g HEC was used.

Fig. 1B shows the effect of $KBrO_3$ concentration used during the polymerization on the apparent viscosity of the resultant composite paste (5% solid content) measured at different shear rates. It is seen that, regardless of the $KBrO_3$ concentration used, the apparent viscosity decreases significantly by increasing the shear rate

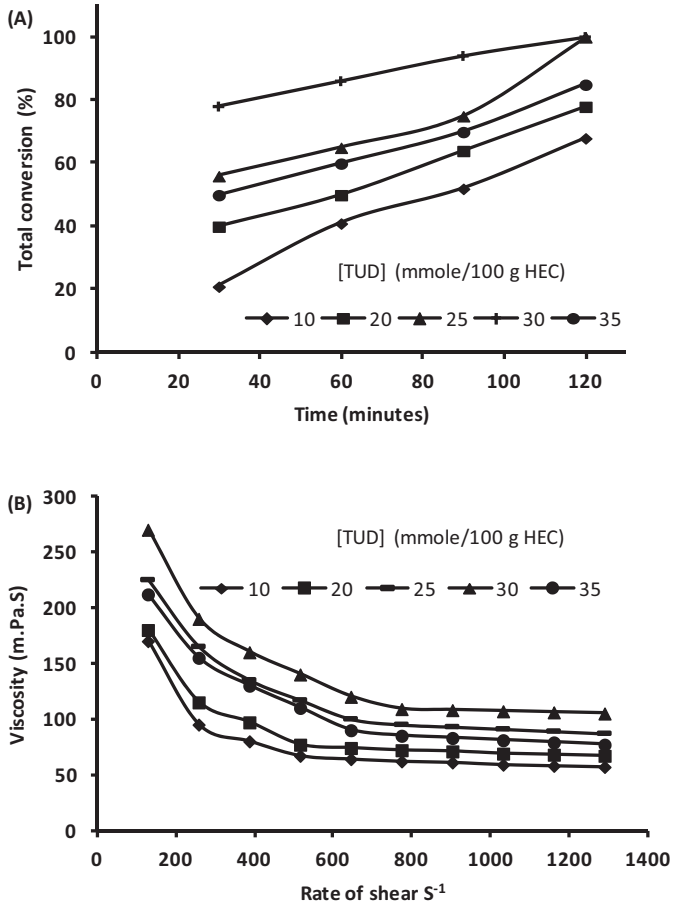


Fig. 2. Effects of TUD concentration on: (A) total conversion and (B) viscosity.

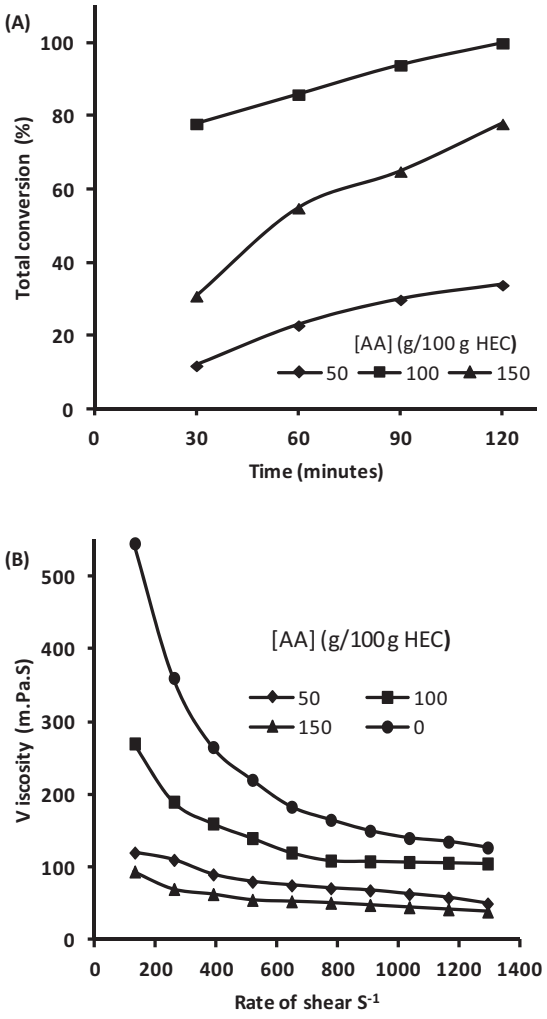


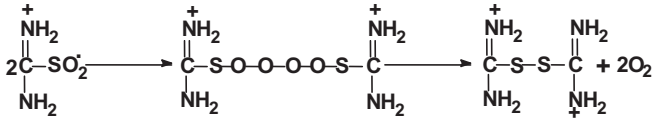
Fig. 3. Effects of acrylic acid concentration on: (A) total conversion and (B) viscosity.

up to 774 S^{-1} then levels off beyond this limit. It is clear also that the apparent viscosity of the composite is lower than that of HEC. The data (Fig. 1B) indicates that the apparent viscosity decreases by increasing $KBrO_3$ concentration. This behavior could be ascribed to the degradative effect of $KBrO_3$ on HEC molecule and the degradation of HEC by Br_2 molecules liberated at higher $KBrO_3$ concentrations (Eq. (6)), in addition to the lower total conversion at higher $KBrO_3$ concentration.

3.3.2. Thiourea dioxide concentration

Fig. 2A shows the effect of TUD concentration on the extent and rate of AA polymerization. The polymerization reaction was carried out at 50 °C for 2 h. using 30 mmol $KBrO_3$/100 g HEC, 100 g AA/100 g HEC, material to liquor ratio 1:10, and 10–35 mmol TUD/100 g HEC. It is seen that, the total conversion of AA to poly(AA) increases by increasing TUD concentration up to 30 mmol/100 g HEC. Further increase in TUD concentration beyond this limit is accompanied by significant decrease in the total conversion.

This behavior indicates that maximum polymerization is obtained when equimolar ratio of both the oxidant and the reductant were used (i.e. $KBrO_3$:TUD is 30:30 mmol/100 g HEC) and this confirms the results obtained above. Increase in the formation of active species (isothiourea dioxide free radicals) may account for the enhancement in the polymerization reaction by increasing TUD concentration up to 30 mmol/100 g HEC. However, by further increasing TUD concentration, the concentration of isothiourea dioxide free radicals is increased to such an extent that they tend to homocombine to give inactive species, rather than to initiate polymerization of AA (Eq. (7)).



(7)

Fig. 2B shows the dependence of the apparent viscosity of the composite paste (5% solid content) on the concentration of TUD used for the polymerization reaction. The results reveal that the viscosity decreases with increasing TUD concentration within range studied. The degradation of the HEC chains due to the effect of the initiation components and the formation of low molecular weight fragments leads to the decrease in the composite viscosity.

3.3.3. Acrylic acid concentration

Fig. 3A shows the relationship between the total conversion percentage and polymerization time when different amounts of acrylic acid were incorporated in the polymerization medium (50%, 100% and 150% based on weight of HEC). The results reveal that, increasing AA concentration from 50% to 100% based on weight of HEC is accompanied by a substantial enhancement in the extent and rate of polymerization. Further increase in AA concentration up to 150% leads to a significant decrease in the extent and rate of polymerization. Enhancement of the polymerization rate is attributed

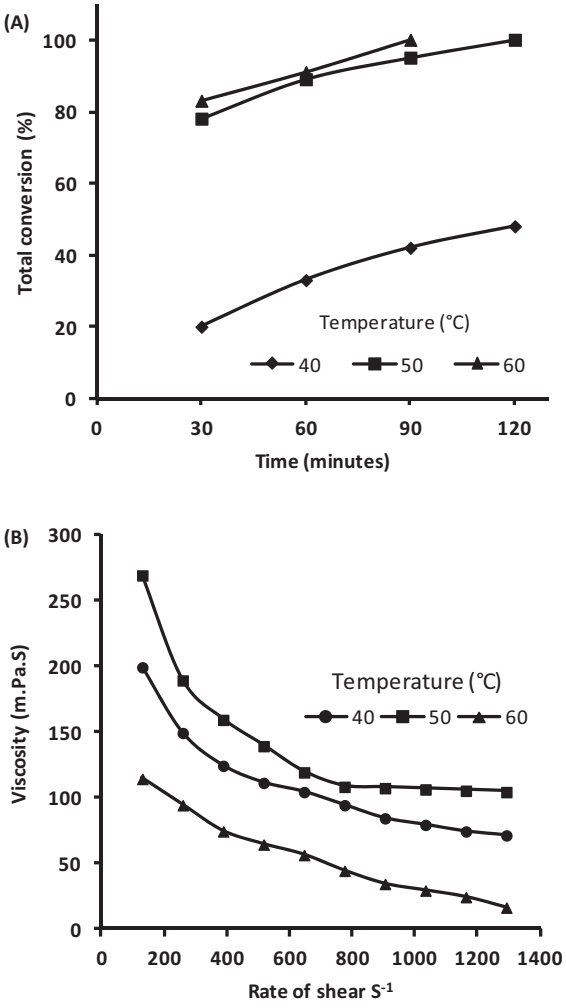


Fig. 4. Effects of polymerization temperature on: (A) total conversion and (B) viscosity.

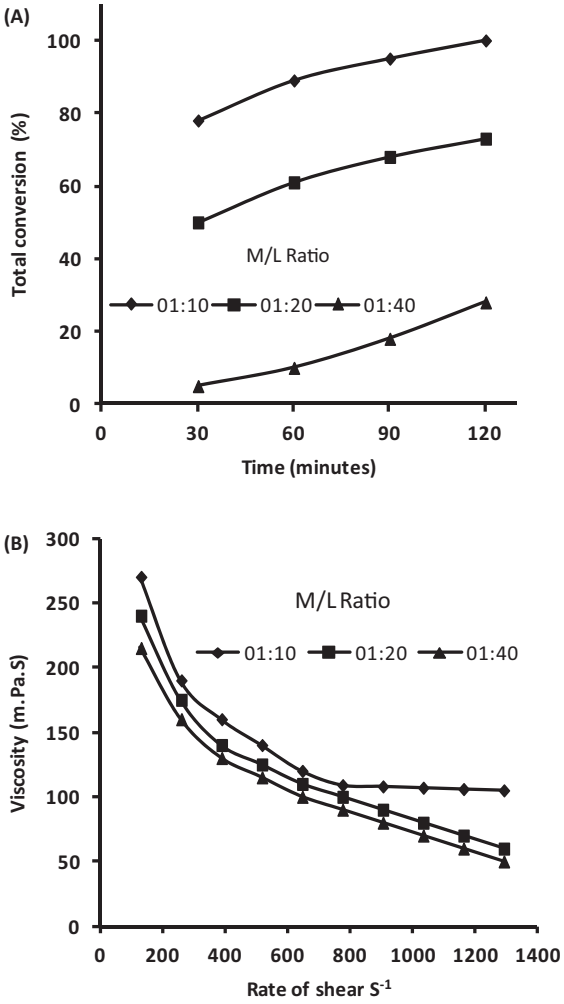


Fig. 5. Effects of material to liquor ration on: (A) total conversion and (B) viscosity.

to the increase in acidity of the polymerization medium as the AA concentration increases. This brings about improvement in $KBrO_3$ efficiency as an oxidizing agent and stabilization of the formation of isothiourea dioxide via the excessive protons present in the polymerization medium (Eq. (1)), this in addition to enhancement of the redox process as a whole. The decrement in the extent and rate of polymerization on using 150% AA may be attributed to shortage in the active species which initiate this amount of AA. Furthermore, liberation of Br_2 at this highly acidic medium leads to oxidation reaction rather than polymerization reaction.

Fig. 3B shows the apparent viscosity of the poly(AA)-HEC composite paste prepared using different AA concentrations as a function of rate of shear. It is evident that the apparent viscosity of the prepared composite is lower than that of the blank HEC. The apparent viscosity of the prepared composites follows the order:

100% AA > 50% AA > 150% AA.

This behavior reflects the effect of the redox system and the acidity of the polymerization medium on the chain length of the poly(AA) (homopolymer and grafted chains) and HEC.

3.3.4. Polymerization temperature

Fig. 4A shows the effect of temperature on the extent and rate of AA polymerization. Monitoring the total conversion of AA during the polymerization reaction shows it to be temperature dependent, following the order: 60 °C > 50 °C > 40 °C. This could be interpreted in terms of the favorable influence of temperature on the efficiency of the redox process, the kinetic energy and diffusibility of AA molecules and/or radicals and the number of collisions between the monomer radicals and monomer molecules.

Fig. 4B demonstrates the influence of the polymerization temperature on the apparent viscosity of the resultant composite paste. The data indicates that apparent viscosity depends on the polymerization temperature and follows the order: 50 °C > 40 °C > 60 °C. The lower viscosity at 60 °C is ascribed to higher rate of termination which leads to shorter poly(AA) chains and the degradative effect of the redox system at high temperatures.

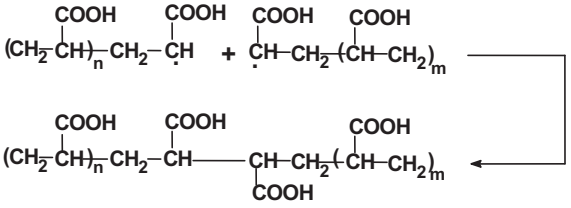
3.3.5. Material to liquor ratio

Fig. 5A shows the effect of material to liquor ratio (M/L ratio) on the extent and rate of AA polymerization with HEC. It is seen that the extent of polymerization depends on the ratio of HEC to the volume of the polymerization medium and follows the order: 1:10 > 1:20 > 1:40. Obviously, the extent of polymerization decreases by increasing the liquor ratio. This could be attributed to the dilution of the reactants in the reaction medium. Dilution reduces molecular collision and, therefore, the opportunity of the molecules of the reactants to undergo polymerization reaction.

Fig. 5B shows the effect of M/L ratio on the apparent viscosity of the resultant poly(AA)-HEC composite paste measured at different rates of shear. It is clear that the apparent viscosity of the composite prepared at lower liquor ratio of 1:10 is higher than that of the

prepared at higher liquor ratios of 1:20 and 1:40. It seems logical that using lower liquor ratio establishes rapid combinations between chains of HEC radicals (R-O•) and poly(AA) radicals (Eqs. (8) and (9)).

$$2R{-}O^{\bullet} \rightarrow R\text{-}O\text{-}O\text{-}R \quad (8)$$



(9)

This chains lengthening is responsible for the increased viscosity at lower liquor ratio.

Acknowledgement

The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding the work through the research group project no. RGP-VPP-029.

References

Abdel-Halim, E. S. (2012a). Physiochemical properties of differently pretreated cellulosic fibers. *Carbohydrate Polymers*, *88*, 1201–1207.

Abdel-Halim, E. S. (2012b). Simple and economic bleaching process for cotton fabric. *Carbohydrate Polymers*, *88*, 1233–1238.

Abdel-Halim, E. S., Abdel-Mohdy, F. A., Al-Deyab, S. S., & El-Newehy, M. H. (2010). Chitosan and monochlorotriazinyl-β-cyclodextrin finishes improve antistatic properties of cotton/polyester blend and polyester fabrics. *Carbohydrate Polymers*, *82*, 202–208.

Abdel-Halim, E. S., Abdel-Mohdy, F. A., Fouda Moustafa, M. G., El-Sawy, S. M., Hamdy Ibrahim, A., & Al-Deyab Salem, S. (2011). Antimicrobial activity of monochlorotriazinyl-β-cyclodextrin/chlorohexidin diacetate finished cotton fabrics. *Carbohydrate Polymers*, *86*, 1389–1394.

Abdel-Halim, E. S., & Al-Deyab, S. S. (2011a). Hydrogel from crosslinked polyacrylamide/guar gum graft copolymer for sorption of hexavalent chromium ion. *Carbohydrate Polymers*, *86*, 1306–1312.

Abdel-Halim, E. S., & Al-Deyab, S. S. (2011b). Low temperature bleaching of cotton cellulose using peracetic acid. *Carbohydrate Polymers*, *86*, 988–994.

Abdel-Halim, E. S., & Al-Deyab, S. S. (2011c). Removal of heavy metals from their aqueous solutions through adsorption onto natural polymers. *Carbohydrate Polymers*, *84*, 454–458.

Abdel-Halim, E. S., & Al-Deyab, S. S. (2011d). Utilization of hydroxypropyl cellulose for green and efficient synthesis of silver nanoparticles. *Carbohydrate Polymers*, *86*, 1615–1622.

Abdel-Halim, E. S., & Al-Deyab, S. S. (2012). Chemically modified cellulosic adsorbent for divalent cations removal from aqueous solutions. *Carbohydrate Polymers*, *87*, 1863–1868.

Abdel-Halim, E. S., El-Rafie, M. H., & Al-Deyab, S. S. (2011). Polyacrylamide/guar gum graft copolymer for preparation of silver nanoparticles. *Carbohydrate Polymers*, *85*, 692–697.

Abdel-Halim, E. S., El-Rafie, M. H., & Kohler, R. (2008). Surface characterization of differently pretreated flax fibers and their application in fiber-reinforced composites. *Polymer: Plastics Technology and Engineering*, *47*, 58–65.

Abdel-Halim, E. S., Emam, H. E., & El-Rafie, M. H. (2008). Utilization of hydroxypropyl cellulose and poly(acrylic acid)-hydroxypropyl cellulose composite as thickeners for textile printing. *Carbohydrate Polymers*, *74*, 938–941.

Abdel-Halim, E. S., Fahmy, H. M., & Fouda, M. M. G. (2008). Bioscouring of linen fabric in comparison with conventional chemical treatment. *Carbohydrate Polymers*, *74*(3), 707–711.

Abdel-Halim, E. S., Fouda, M. G., Hamdy, I. A., Abdel-mohdy, F. A., & El-sawy, S. M. (2010). Incorporation of chlorohexidin diacetate into cotton fabrics grafted with glycidyl methacrylate and cyclodextrin. *Carbohydrate Polymers*, *79*, 47–53.

Abdel-Halim, E. S., Konczewicz, W., Zimniewska, M., Al-Deyab, S. S., & El-Newehy, M. H. (2010). Enhancing hydrophilicity of bioscoured flax fabric by emulsification post-treatment. *Carbohydrate Polymers*, *82*, 195–201.

Abdel-Mohdy, F. A., Abdel-Halim, E. S., Abu-Ayana, Y. M., & El-Sawy, S. M. (2009). Rice straw as a new resource for some beneficial uses. *Carbohydrate Polymers*, *75*, 44–51.

Brendel, O., Iannetta, P. P. M., & Stewart, D. (2000). A rapid and simple method to isolate pure alpha-cellulose. *Phytochemical Analysis*, *11*, 7–10.

Chen, L., Ni, Y., Bian, X., Qiu, X., Zhuang, X., Chen, X., et al. (2005). A novel approach to grafting polymerization of 3-caprolactone onto starch granules. *Carbohydrate Polymers*, *60*, 103–109.

da Silva, D. A., de Paula, R. C. M., & Feitosa, J. P. A. (2007). Graft copolymerization of acrylamide onto cashew gum. *European Polymer Journal*, *43*, 2620–2629.

Dal-Bó, A. G., Laus, R., Felippe, A. C., Zanette, D., & Minatti, E. (2011). Association of anionic surfactant mixed micelles with hydrophobically modified ethyl(hydroxyethyl)cellulose. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *380*, 100–106.

El-Tahlawy, Kh. F., Abdel-Halim, E. S., Hudson, S. M., & Hebeish, A. A. (2007). The acylation of imino chitosan: its effect on blending with cellulose acetate. *Journal of Applied Polymer Science*, *104*, 727–734.

Fahmy, H. M., & Abdel-Halim, E. S. (2010). Utilization of poly(N-vinyl-2-pyrrolidone) to enhance the performance and antibacterial properties as well as UV protection of ester crosslinked cotton fabrics. *Journal of Industrial Textiles*, *40*, 109–121.

Geresh, S., Gdalevsky, G. Y., Gilboa, I., Voorspoels, J., Remon, J. P., & Kost, J. (2004). Bioadhesive grafted starch copolymers as platforms for peroral drug delivery: A study of theophylline release. *Journal of Controlled Release*, *94*, 391–398.

Gong, H., Liu, M., Zhang, B., Cui, D., Gao, C., Ni, B., et al. (2011). Synthesis of oxidized guar gum by dry method and its application in reactive dye printing. *International Journal of Biological Macromolecules*, *49*, 1083–1091.

Gorgieva, S., & Kokol, V. (2011). Synthesis and application of new temperature-responsive hydrogels based on carboxymethyl and hydroxyethyl cellulose derivatives for the functional finishing of cotton knitwear. *Carbohydrate Polymers*, *85*, 664–673.

Gurgel, L. V. A., de Freitas, R. P., & Gil, L. F. (2008). Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by sugarcane bagasse and mercerized sugarcane bagasse chemically modified with succinic anhydride. *Carbohydrate Polymers*, *74*, 922–929.

Hanley, S. J., Revol, J. F., Godbout, L., & Gray, D. G. (1997). Atomic force microscopy and transmission electron microscopy of cellulose from *Micrasterias denticulata*; evidence for a chiral helical microfibril twist. *Cellulose*, *4*, 209–220.

Hashem, A., Abdel-Halim, E. S., El-Tahlawy, Kh. F., & Hebeish, A. A. (2005). Enhancement of Co(II) and Ni(II) adsorption from aqueous solutions onto peanut hull through esterification using citric acid. *Adsorption Science and Technology*, *23*, 367–380.

Hashem, A., Abdel-Halim, E. S., & Sokker, H. H. (2007). Bi-functional starch composites prepared by γ-irradiation for removal of anionic and cationic dyes from aqueous solutions. *Polymer: Plastics Technology and Engineering*, *46*, 71–77.

Hashem, A., Sokkar, H. H., Abdel-Halim, E. S., & Gamal, A. (2005). γ-Induced graft copolymerization onto cellulosic fabric waste for cationic dye removal. *Adsorption Science and Technology*, *23*, 455–465.

Hebeish, A., Abd El-Thalouth, I., El-Kashouti, M. A., & Abdel-Fattah, S. H. (2003). Graft copolymerization of acrylonitrile onto starch using potassium permanganate as initiator. *Angewandte Makromolekulare Chemie*, *78*, 101–108.

Hebeish, A., El-Rafie, M. H., Abdel-Mohdy, F. A., Abdel-Halim, E. S., & Emam, H. E. (2010). Carboxymethyl cellulose for green synthesis and stabilization of silver nanoparticles. *Carbohydrate Polymers*, *82*, 933–941.

Hebeish, A., Higazy, A., El-Shafei, A., & Sharaf, S. (2010). Synthesis of carboxymethyl cellulose (CMC) and starch-based hybrids and their applications in flocculation and sizing. *Carbohydrate Polymers*, *79*, 60–69.

Hebeish, A., Ramadan, M., Abdel-Halim, E. S., & Abo-Okeil, A. (2011). An effective adsorbent based on sawdust for removal of direct dye from aqueous solutions. *Clean Technologies and Environmental Policy*, *13*, 713–718.

Ibrahim, N. A., Abdel Moneim, N. M., Abdel Halim, E. S., & Hosni, M. M. (2008). Pollution prevention of cotton-cone reactive dyeing. *Journal of Cleaner Production*, *16*, 1321–1326.

Joshi, J. M., & Sinha, V. K. (2007). Ceric ammonium nitrate induced grafting of polyacrylamide onto carboxymethyl chitosan. *Carbohydrate Polymers*, *67*, 427–435.

Kaith, B. S., Singha, A. S., & Kalia, S. (2007). Grafting MMA onto flax under the influence of microwave radiation and the use of flax-g-poly (MMA) in preparing PF composites. *Autex Research Journal*, *7*, 119–129.

Kang, H. M., Cai, Y. L., & Liu, P. S. (2006). Synthesis, characterization and thermal sensitivity of chitosan-based graft copolymers. *Carbohydrate Research*, *11*, 2851–2855.

Knauf, M., & Moniruzzaman, M. (2004). Lignocellulosic biomass processing: a perspective. *International Sugar Journal*, *106*, 147–150.

Kugge, C., Craig, V. S. J., & Daicic, J. (2004). A scanning electron microscope study of the surface structure of mineral pigments, lattices and thickeners used for paper coating on non-absorbent substrates. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *238*, 1–11.

Ly, E. B., Bras, J., Sadocco, P., Belgacem, M. N., Dufresne, A., & Thielemans, W. (2010). Surface functionalization of cellulose by grafting oligoether chains. *Materials Chemistry and Physics*, *120*, 438–445.

Masuhiro, T., Shafiul, I., Takayuki, A., Alessandra, B., & Giuliano, F. (2005). Microwave irradiation technique to enhance protein fibre properties. *Autex Research Journal*, *5*, 40–48.

Meshram, M. W., Patil, V. V., Mhaske, S. T., & Thorat, B. N. (2009). Graft copolymers of starch and its application in textiles. *Carbohydrate Polymers*, *75*, 71–78.

Mohamed, Z. E., Amr, A., Knittel, D., & Schollmeyer, E. (2010). Synthesis and application of new sizing and finishing additives based on carboxymethyl cellulose. *Carbohydrate Polymers*, *81*, 769–774.

Patural, L., Marchal, P., Govin, A., Grosseau, P., Ruot, B., & Devès, O. (2011). Cellulose ethers influence on water retention and consistency in cement-based mortars. *Cement and Concrete Research*, *41*, 46–55.

Rui-He, Y., Wang, X., Wang, Y., Yang, K., Zeng, J., & Ding, S. (2006). A study on grafting poly(1,4-dioxan-2-one) onto starch via 2,4-tolylene diisocyanate. *Carbohydrate Polymers*, *65*, 28–34.

Sailaja, G., & Murthy, R. R. (2010). kinetics of polymerization of methylmethacrylate initiated by the Mn(III)-citric acid redox system. *Rasayan Journal of Chemistry*, *3*, 321–327.

Shaikh, H. M., Pandare, K. V., Nair, G., & Varma, A. J. (2009). Utilization of sugarcane bagasse cellulose for producing cellulose acetates: Novel use of residual hemicellulose as plasticizer. *Carbohydrate Polymers*, *76*, 23–29.

Singh, V., Tiwari, A., Pandey, S., & Singh, S. K. (2007). Peroxydisulfate initiated synthesis of potato starch-graft-poly (acrylonitrile) under microwave irradiation. *Express Polymer Letters*, *1*, 51–58.

Singh, V., Tiwari, A., & Sanghi, R. (2005). Studies on $K_2S_2O_8$/ascorbic acid initiated synthesis of Ipomoea dasysperma seed gum-g-poly(acrylonitrile): A potential industrial gum. *Journal of Applied Polymer Science*, *98*, 1652–1662.

Sokkar, H. H., Abdel-Halim, E. S., Aly, A. S., & Hashem, A. (2004). Cellulosic fabric wastes grafted with DMAEMA for removal of direct dyes. *Adsorption Science and Technology*, *22*, 679–691.

Sun, R. C., & Hughes, S. (1998). Fractional extraction and physico-chemical characterization of hemicelluloses and cellulose from sugar beet pulp. *Carbohydrate Polymers*, *36*, 293–299.

Szamel, G., Domjan, A., Klebert, S., & Pukanszky, B. (2008). Molecular structure and properties of cellulose acetate chemically modified with caprolactone. *European Polymer Journal*, *44*, 357–365.

Turk, S. S., & Schneider, R. (2000). Printing properties of a high substituted guar gum and its mixture with alginate. *Dyes and Pigments*, *47*, 269–275.

Vahdat, A., Bahrami, H., Ansari, N., & Ziaie, F. (2007). Radiation grafting of styrene onto polypropylene fibres by a 10 MeV electron beam. *Radiation Physics and Chemistry*, *76*, 787–793.

Vieira, J. G., de Carvalho Oliveira, G., Filho, G. R., de Assunção, R. M. N., da Silva Meireles, C., Cerqueira, D. A., et al. (2009). Production, characterization and evaluation of methylcellulose from sugarcane bagasse for applications as viscosity enhancing admixture for cement based material. *Carbohydrate Polymers*, *78*, 779–783.

Wang, J. P., Chen, Y. Z., Zhang, S. J., & Yu, H. Q. (2008). A chitosan-based flocculant prepared with gamma-irradiation-induced grafting. *Bioresource Technology*, *99*, 3397–3402.

Wang, Z. M., Li, L., Xiao, K. J., & Wu, J. Y. (2009). Homogeneous sulfation of bagasse cellulose in an ionic liquid and anticoagulation activity. *Bioresource Technology*, *100*, 1687–1690.

Yu, H., Liu, R. G., Shen, D. W., Jiang, Y., & Huang, Y. (2005). Study on morphology and orientation of cellulose in the vascular bundle of wheat straw. *Polymer*, *46*, 5689–5694.

Zahran, M. K., Abdel-Halim, E. S., & El-Rafie, M. H. (1998). Utilization of corn stalks for preparation of hydroxyethyl cellulose. *Colourage*, *45*, 19–26.

Zhu, J., Dong, X., Wang, X., & Wang, Y. (2010). Preparation and properties of a novel biodegradable ethyl cellulose grafting copolymer with poly(p-dioxanone) side-chains. *Carbohydrate Polymers*, *80*, 350–359.