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Preparation and characterization of water soluble poly(acrylic acid)–hydroxypropyl cellulose composite

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ABSTRACT

Purified flax waste was obtained from flax processing wastes via subjecting the latter to alkali treatment followed by peracetic acid bleaching. The so obtained purified flax wastes were chemically modified via reacting with propylene oxide in alkaline medium. The resultant hydroxypropyl cellulose (HPC) was incorporated in a polymerization medium containing acrylic acid and potassium bromate/thiourea mixture as initiation system. The polymerization reaction was monitored by determining the total conversion percent and the rheological properties of the resultant polyacrylic acid–hydroxypropyl cellulose composite [poly(AA)–HPC]. Results obtained indicate that the optimum conditions of polymerization process were: 12 mmole $KBrO_3$, 4 mmole thiourea and 100 g acrylic acid/100 g HPC at 50 °C for 2 h using a material to liquor ratio of 1:5.

1. Introduction

Grafting of different vinyl monomers onto polysaccharides has been extensively studied many years ago with the aim of obtaining different functional products. Composite is a term given to the products of graft copolymerization reaction of polysaccharide and vinyl monomer in the presence of initiator (Buyanov, Revelskaya, Bobrova, & Elyashevich, 2006; Ghanshyam, Lalit, & Rajeev, 2005; Ohno, Yoshizawa, Miyashita, & Nishio, 2005; Okrasa, Boiteux, Ulanski, & Seytre, 2001; Samaha, Nasr, & Hebeish, 2005).

These graft copolymerization reactions have been carried out by different initiation techniques such as gamma irradiation (Lu, Yi, Li, & Ha, 2001; Palacios, Aliev, & Burillo, 2003; Turmanova, Godjevargova, & Vasileva, 2005; Yu & Lee, 2007) and chemical initiation (Gupta & Khandekar, 2003; Gurdag, Guclu, & Ozgumus, 2001; Shoinbekova, Nikitina, Zhunusova, Mukhitdinova, & Ergozhin, 2005; Yu & Huang, 2006).

Modifications of cellulose and its derivatives by grafting of different vinyl monomers gives new materials for composite membranes (Buyanov et al., 2006), metal ion sorption and enzyme immobilization (Ghanshyam et al., 2005; Yu & Huang, 2006).

Flax processing wastes contain complex mixture of cellulose and different cementing materials like hemicelluloses, pectins and lignins, in addition to minor amounts of fats and waxy materials. This research work is directed towards the use of chemical methods to convert flax processing wastes to valuable industrial products. The main purpose of this work is to achieve: (a) preparation of water soluble composite through grafting of acrylic acid onto hydroxypropyl cellulose (HPC) using $KBrO_3$/thiourea redox system, (b) studying the major factors affecting the preparation of poly(AA)–HPC composite and (c) evaluating the properties of the poly(AA)–HPC composite.

2. Experimental

2.1. Materials

Sodium hydroxide, glacial acetic acid, hydrogen peroxide, nonionic wetting agent, isopropyl alcohol, propylene oxide, acetone, acrylic acid, thiourea (TU), potassium bromate, potassium bromide, potassium iodide, sulfuric acid, sodium thiosulfate and hydroquinone were laboratory grade reagents.

2.2. Preparation of HPC

Flax wastes were subjected to alkali treatment followed by bleaching with peracetic acid. The so obtained purified flax waste was used as a starting material for the preparation of HPC. Details of HPC preparation are given elsewhere (El-Rafie, Abdel-Halim, & Emam, 2007).

2.3. Preparation of poly(AA)–HPC composite

Unless other wise stated, polymerization of acrylic acid with HPC was carried out as follows:

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HPC dissolved in water was stirred well and the temperature was raised to the desired polymerization temperature. When the reaction temperature was attained, known concentrations of acrylic acid and aqueous solution of the initiation components (potassium bromate/thiourea) were added to the HPC solution. A material to liquor ratio of 1:5 was employed and the reaction was allowed to proceed under continuous stirring for 2 h.

Details of the polymerization conditions are given in the text. The magnitude of polymerization was determined as percentage total conversion via estimation of the residual double bonds (Wallace & Young, 1966).

2.4. Testing and analysis

2.4.1. Percent total conversion

The percent total conversion was calculated via quantitative estimation of the double bonds of the monomer used before and during polymerization according to a reported method (Wallace & Young, 1966).

2.4.2. Apparent viscosity

The intrinsic viscosity was determined according to the general procedure described elsewhere (Kurata, Tsunashima, Iwama, & Kamada, 1975, chap. IV).

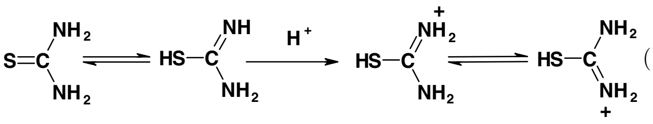
3. Results and discussion

3.1. Preparation of poly(AA)–HPC composite

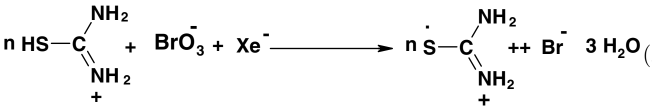
The HPC obtained from bleached flax wastes was subjected to further chemical modification via reaction with acrylic acid, in presence of potassium bromate/thiourea initiation system. It seems logical to shed some insight on the mechanisms involved in the polymerization reaction using the said initiation system.

3.2. Tentative mechanism

When potassium bromate (oxidant) is coupled with thiourea (reductant), in acidic medium, a very efficient redox system is established. In presence of acrylic acid as monomer and HPC which contains functional hydroxyl groups in the cellulose structure, the primary free radical species brought about by decomposition of the redox system can initiate homopolymerization of acrylic acid as well as grafting of the latter onto the HPC molecules. Specifically the polymerization process involves conversion of thiourea, in acidic medium, to isothiourea as shown by Eq. (1). The generation of a free radical in this system takes place by two routs. (i) Abstract the reactive hydrogen attached to the sulfur atom in isothiourea by the bromate anion as shown by Eq. (2).



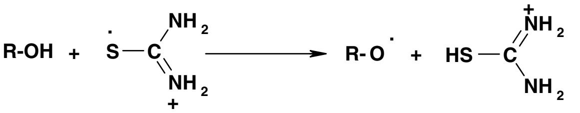
$$S{=}C(NH_2)_2 \rightleftharpoons HS{-}C({=}NH)NH_2 \xrightarrow{H^+} HS{-}C({=}\overset{+}{N}H_2)NH_2 \rightleftharpoons HS{-}C(NH_2){=}\overset{+}{N}H_2 \quad (1)$$



$$n\,HS{-}C(NH_2){=}\overset{+}{N}H_2 + BrO_3^- + Xe^- \longrightarrow n\,\dot{S}{-}C(NH_2){=}\overset{+}{N}H_2 ++ Br^- \; 3\,H_2O \quad (2)$$

where $X = n - 6$ is the number of electron contributed from the reaction mechanism.

The isothiourea radicals attack functional hydroxyl groups of (HPC) to form HPC free radicals as illustrated by Eq. (3).



$$R{-}OH + \dot{S}{-}C(NH_2){=}\overset{+}{N}H_2 \longrightarrow R{-}O^{\bullet} + HS{-}C({=}\overset{+}{N}H_2)NH_2 \quad (3)$$

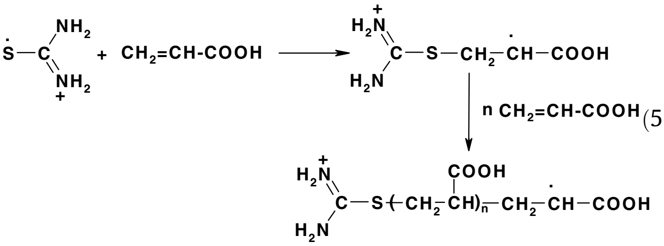
(ii) Abstraction of hydrogen atom by the bromate anion from HPC to form HPC free radicals as illustrated by Eq. (4).

$$6R\text{-}OH + BrO_3^- \rightarrow 6R\text{-}O^{\bullet} + Br^- + 3H_2O. \quad (4)$$

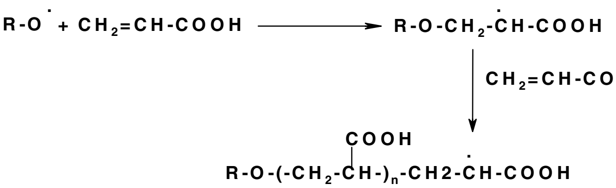
Comparing abstraction of H-atom in the routes (i) and (ii), it is logically to confess that the weak covalent bonding between the S-atom and the H-atom in isothiourea molecule will greatly facilitate abstraction of hydrogen atoms from the thiol group by bromate anions [route (i)]. Accordingly the route (i) seems to be the main source of free radical generation.

Furthermore, isothiourea can strongly initiate homopolymerization of acrylic acid molecules (Eq. (5)). The reaction of HPC free radical with acrylic acid initiates the grafting reaction along the HPC back bone (Eq. (6)).

It should be mentioned that $KBrO_3$ plays an important role other than initiating acrylic acid polymerization, namely oxidation of HPC molecules, particularly at higher bromate concentration. Furthermore, the Br_2 molecules liberated at higher bromate concentration (Eq. (7)) may also attack and oxidize the HPC which lead to subsequent degradation of HPC molecules.

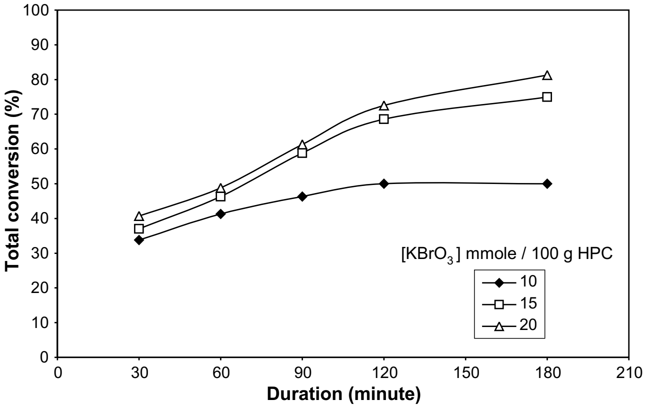


$$\dot{S}{-}C(NH_2){=}\overset{+}{N}H_2 + CH_2{=}CH{-}COOH \longrightarrow H_2\overset{+}{N}{=}C(H_2N){-}S{-}CH_2{-}\dot{C}H{-}COOH \xrightarrow{n\,CH_2=CH-COOH} H_2\overset{+}{N}{=}C(H_2N){-}S{\left(CH_2{-}\underset{COOH}{CH}\right)_n}{-}CH_2{-}\dot{C}H{-}COOH \quad (5)$$



$$R{-}O^{\bullet} + CH_2{=}CH{-}COOH \longrightarrow R{-}O{-}CH_2{-}\dot{C}H{-}COOH \xrightarrow{CH_2=CH-COOH} R{-}O{-}({-}CH_2{-}\underset{COOH}{CH}{-})_n{-}CH2{-}\dot{C}H{-}COOH \quad (6)$$

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow BrO_2 + 3H_2O. \quad (7)$$



100 g acrylic acid: /100 g HPC;
material to liquor ratio; 1: 5, temperature: 50 °C

Fig. 1. Effect of $KBrO_3$ concentration in absence of thiourea on the total conversion.

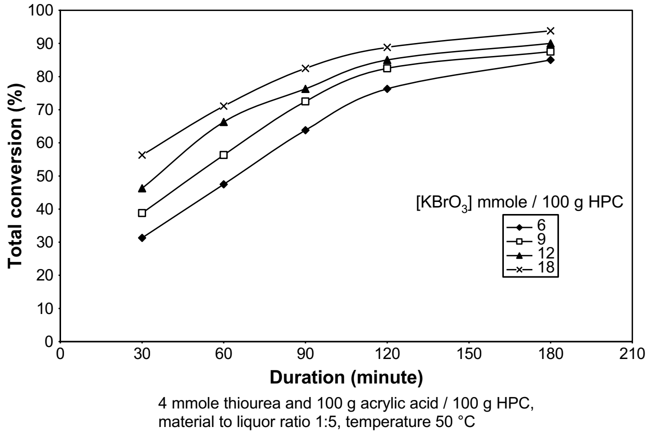


Fig. 2. Effect of $KBrO_3$ concentration in presence of thiourea on the total conversion.

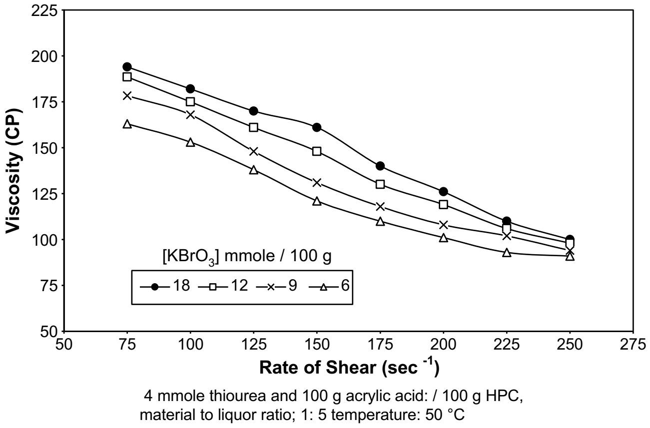


Fig. 3. Effect of $KBrO_3$ concentration on the apparent viscosity.

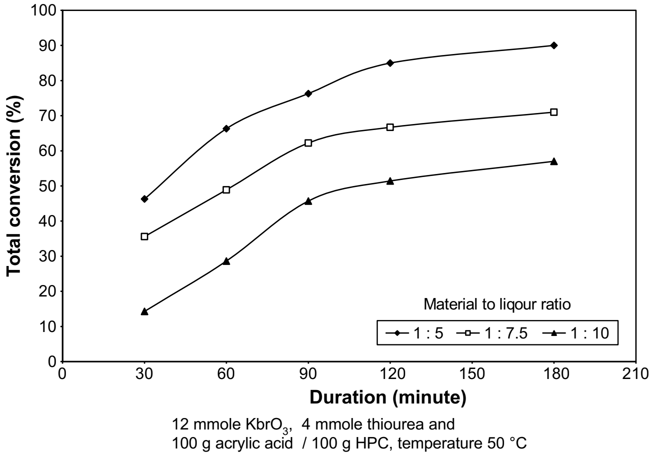


Fig. 5. Effect of material to liquor ratio on the total conversion.

3.3. Effect of initiator concentration

Fig. 1 shows the effect of $KBrO_3$ concentration as initiator, in absence of thiourea on the total conversion during grafting of acrylic aid onto HPC. It is clear that by increasing the $KBrO_3$ concentration from 10 mmole to 20 mmole/100 g HPC the percent total conversion (TC%) increases and reaches 80% after 3 h. The increment in the TC% could be ascribed to the enhancement in the formation of HPC macroradicals at higher $KBrO_3$ concentration (Eq. (4)).

Fig. 2 shows the dependence of the extent and rate of polymerization of acrylic acid, expressed as percent total conversion, on $KBrO_3$ (oxidant) concentration in presence of thiourea. The polymerization reaction was carried out using 6–18 mmole $KBrO_3$, 4 mmole thiourea and 100 g acrylic acid/100 g HPC at 50 °C for 3 h using a material to liquor ratio of 1:5. It is observed from Fig. 2 that regardless the $KBrO_3$ concentration used, the total conversion increases significantly by increasing the reaction duration up to 120 min. Further increase above this limit is accompanied by marginal increment in the TC%. The data indicates also that increasing $KBrO_3$ concentration from 6 to 18 mmole/100 g HPC leads to enhancement in the TC%.

Fig. 3 shows the effect of $KBrO_3$ concentration used during the polymerization on the apparent viscosity of the resultant composite (10% solid content) measured at different shear rates. It seems that regardless of the $KBrO_3$ concentration used, the apparent viscosity decreases significantly by increasing the shear rates up to $150\ s^{-1}$. The data (Fig. 3) indicates that the apparent viscosity decreases by increasing $KBrO_3$ concentration. This behavior could be ascribed to the degradation effect of $KBrO_3$ on HPC molecule and increase in the rate of termination reaction which leads to the formation of short polymer chains.

3.4. Effect of acrylic acid concentration

Fig. 4 shows the relationship between the total conversion percentage and polymerization reaction duration when different concentrations of acrylic acid were incorporated in the polymerization medium (50%, 100% and 150% based on weight of HPC). The results reveal that increasing acrylic acid concentration from 50% to 100%

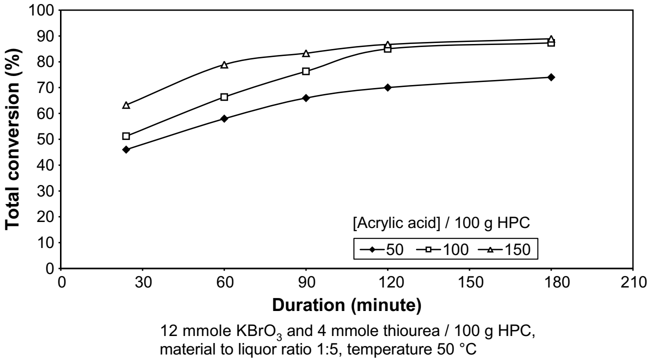


Fig. 4. Effect of acrylic acid concentration on the total conversion.

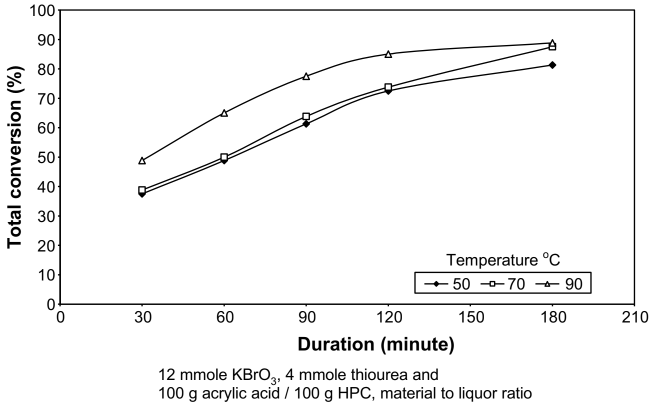


Fig. 6. Effect of temperature on the total conversion.

based on weight of HPC is accompanied by substantial enhancement in the extent and rate of polymerization. Further increase in acrylic aid concentration more than 100% leads to a marginal increase in the total conversion. The enhancement in the polymerization reaction is attributed to the increase in acidity of the polymerization medium as the acrylic acid concentration increases. This brings about: (a) improvement of $KBrO_3$ efficiency as an oxidizing agent, (b) stabilization of the formation of isothiourea dioxide via the excessive protons present in the polymerization medium (Eq. (1)) and (c) enhancement of the redox process as a whole. The marginal increment in the extent and rate of polymerization on using 150% acrylic acid may be attributed to shortage in the active species which initiate this amount of acrylic acid. Furthermore, liberation of Br_2 at this highly acidic medium leads to oxidation reaction rather than polymerization reaction.

3.5. Effect of material to liquor ratio

Fig. 5 shows the effect of material to liquor ration on the extent and rate of acrylic acid polymerization with HPC. It is seen that the extent of polymerization depends on the ratio of HPC to the volume of the polymerization medium and follows the order:

$$1:5 > 1:7.5 > 1:10.$$

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.

3.6. Effect of temperature

Fig. 6 shows the effect of temperature on the extent and rate of acrylic acid polymerization. Monitoring the total conversion of acrylic acid during the polymerization reaction indicates that increasing the initial temperature of the polymerization medium leads to gradual enhancement in the rate of polymerization. This could be interpreted in terms of the favorable influence of temperature on, (a) efficiency of redox process, (b) the kinetic energy and diffusibility of acrylic acid molecules and/or radicals and (c) the increasing number of collisions between the monomer radicals and monomer molecules.

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